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PROCEEDINGS
OF THE
INDIAN ACADEMY OF SCIENCES

VOL. III

SECTION A

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CONTENTS

Vol. III—SECTION A

No. 1—January, 1936

	PAGE
First Annual Meeting of the Indian Academy of Sciences.—Presidential Address. By C. V. RAMAN, Kt., F.R.S., N.L.	1
Unitary Theory of Field and Matter. I. Classical Treatment. Charged Particle with Magnetic Rest-Moment. By MAX BORN	8
The Raman Spectra of Ortho-Phosphoric Acid and Some Phosphates. By C. S. VENKATESWARAN	25
The Occurrence of Furan Derivatives in Volatile Oils—III. β -Clausenan and γ -Clausenan. By B. SANJIVA RAO and K. S. SUBRAMANIAM	31
Brucine Sulphate as an Internal Indicator in Titrations with Standard Dichromate Solution. By D. S. NARAYANAMURTHI and T. R. SESHADRI	38
Optic Moments of Organic Molecules in Relation to Crystalline and Magnetic Birefringence. By M. RAMANADHAM	43
Vinogradov's Solution of Waring's Problem (II). By I. CHOWLA	51
The Raman Spectra of Some Organic Liquids under High Dispersion and Resolving Power. (Benzene, Toluene, Phenol, Chlorobenzene, Pyridine and Cyclohexane.) By R. ANANTHAKRISHNAN	52
The Diffraction of Light by High Frequency Sound Waves: Part III. Doppler Effect and Coherence Phenomena. By C. V. RAMAN and N. S. NAGENDRA NATH	75

No. 2—February, 1936

Unitary Theory of Field and Matter. II. Classical Treatment. Charged Particle with Electric and Magnetic Moment. By MAX BORN	85
The Measurement of the Transmission of Heat by Convection from Insolated Ground to the Atmosphere. By P. K. RAMAN	98
Studies in Thorium Phosphate Gels. By M. U. PARMAR, S. M. MEHTA and MATA PRASAD	107
The Diffraction of Light by High Frequency Sound Waves: Part IV. Generalised Theory. By C. V. RAMAN and N. S. NAGENDRA NATH	119
Molecular Clustering in Liquid Fatty Acids. By R. S. KRISHNAN	126
Deformation Frequencies in the Raman Spectra of Linear Molecules: Acetylene. By S. BHAGAVANTAM and A. VEERABHADRA RAO	135
Intensities in the Bands of the Violet Cyanogen System. By DR. N. R. TAWDE, B.A., M.Sc. (Bom.), Ph.D. (Lond.), A.Inst.P. (Lond.)	140

	PAGE
The Absorption Spectra of Some Aromatic Compounds. Part I.—Hydrocarbons. By P. K. SESHAN	148
The Absorption Spectra of Some Aromatic Compounds. Part II.—Quinones and Hydroquinones By P. K. SESHAN	172
Diamagnetic Susceptibility of Sulphuric Acid-Water Mixture. By B. NAGESHA RAO	188

No. 3—March, 1936

On the Numbers of Ward and Bernoulli. By HANSRAJ GUPTA ..	193
Polarisation of the Raman Bands of Water and Deuterium Oxide. By R. ANANTHAKRISHNAN	201
Antiseptics and Anthelmintics. Part II. A Synthesis of 6-Benzyl-7-hydroxyflavone and 6- <i>n</i> -Hexyl-7-hydroxyflavone. By D. R. DHINGRA, HARMINDER LAL UPPAL and K. VENKATARAMAN ..	206
Scattering of Light in Optical Glasses. By R. S. KRISHNAN ..	211
Gravity Formulæ in Geodesy; Their Precision and Interpretation. By B. L. GULATEE, M.A. (CANTAB.)	221
Derivatives of Salicylic Acid—Part IX. Stability of the Sulphonic Acid Group in the 4-Sulphosalicylic Acid. Part I. Nitration of 4-Sulphosalicylic Acid. By N. W. HIRWE and M. R. JAMBHEKAR ..	236
Studies on the Anisotropy of the Optical Polarisation Field in Liquids. Part I. By B. SUNDARA RAMA RAO	240
Studies on the Anisotropy of the Optical Polarisation Field in Liquids. Part II. By B. SUNDARA RAMA RAO	244
The Alkaloids of Holarrhena Anti-Dysenterica Part IV. The Occurrence of Two Further New Bases in the Bark of Indian Holarrhena and their Relationship to Conessine and Holarrhimine. By SALIMUZZAMAN SIDDIQUI	249
The Alkaloids of Holarrhena Anti-Dysenterica Part V. Studies in Holarrhimine. By SALIMUZZAMAN SIDDIQUI and RAFAT HUSAIN SIDDIQUI	257
Derivatives of Salicylic Acid—Part X. Stability of Sulphonic Acid Group in the 4-Sulphosalicylic Acid. Part II.—Bromination of 4-Sulphosalicylic Acid. By N. W. HIRWE and M. R. JAMBHEKAR ..	261
The Tracks of the α -Particles of Thorium and Its Products. By H. J. TAYLOR, M.Sc., and V. D. DABHOLKAR, M.Sc. ..	265
On the Theory of Pressure Broadening of Spectral Lines. By EDWIN GORA	272
Ultrasonic Velocities in Some Organic Liquids—Part II. By S. PARTHASARATHY	285
Physical Principles and Applications of Magneto-Chemistry by Prof. S. S. Bhatnagar and Dr. K. N. Mathur. (C. V. RAMAN) ..	290

No. 4—April, 1936

Geometrical Inversion in the Acids Derived from the Coumarins. Part II.	
<i>Cis to Trans.</i> By T. R. SESHADRI and P. SURYAPRAKASA RAO ..	293
Ultrasonic Velocities in Liquid Mixtures. By S. PARTHASARATHY ..	297
On a Function connected with the Singular Series.	
By K. SAMBASIVA RAO	301
The Raman Spectrum and Electrolytic Dissociation of Selenic Acid.	
By C. S. VENKATESWARAN	307
The Neutrino Theory of Light. By MAX BORN and N. S. NAGENDRA	
NATH	318
On the Error Term in a Certain Sum.	
By M. L. N. SARMA, B.A. (HONS.)	338
Pillai's Exact Formula for the Number $g(n)$ in Waring's Problem	
By S. CHOWLA	339
Pillai's Exact Formula for the Number $g(n)$ in Waring's Problem.	
By BROJOMOHAN PADHY	341
On the Band Systems and Structure of SiF. By R. K. ASUNDI and	
R. SAMUEL	346
The Design of Falls with Reference to Uplift Pressure. By GURDAS	
RAM, M.Sc., and V. I. VAIDHIANATHAN, D.Sc., F. Inst. P ..	360
Studies on the Anisotropy of the Optical Polarisation Field in	
Liquids—Part III. By B. SUNDARA RAMA RAO	369
Variation of Intensity of Scattered Light with Temperature.	
By CH. V. JOGARAO	377
Refractivity and Magnetic Birefringence of Liquid Mixtures.	
By M. RAMANADHAM	381

No. 5—May, 1936

Absorption Spectra of Tetra-Alkyl Ammonium Salts. Contributions to	
the Theory of Co-ordinate Linkage IX. By SH. NAWAZISH ALI	
and R. SAMUEL	399
Magnetic Susceptibilities of Some Organic Compounds in Different	
Physical States. By K. C. SUBRAMANIAM	420
Magnetic Studies of Sulphur and Some Sulphur Compounds. By	
P. S. VARADACHARI and K. C. SUBRAMANIAM	428
Vortex Motion in Rectangular Cylinders. By B. R. SETH	435
Diffraction of Light by Ultrasonic Waves. By S. PARTHASARATHY ..	442
Neutrinos and Light Quanta. By N. S. NAGENDRA NATH	448
The Diffraction of Light by High Frequency Sound Waves: Part V.	
General Considerations—Oblique Incidence and Amplitude Changes.	
By C. V. RAMAN and N. S. NAGENDRA NATH	459
Electronic Configuration and Bond Energy. By R. K. ASUNDI and	
R. SAMUEL	466

Ultrasonic Velocities in Organic Liquids. Part III.—Esters and Ethers. By S. PARTHASARATHY	482
On the Absorption Spectra and Linkage of Inorganic Nitrates and Sulphates in the Vapour State. By MOHD. ISRARUL HAQ and R. SAMUEL	487

No. 6—June, 1936

Lipins of Fenugreek (<i>Trigonella fœnum græcum.</i>). By B. N. SSTEI, M.Sc., A.I.C., A.I.I.Sc., and M. SREENIVASAYA, B.A., F.I.I.Sc. ..	513
Ultrasonic Velocities in Organic Liquids. Part IV.—Halogen Compounds. By S. PARTHASARATHY	519
Upon Some New Results in the Domain of Non-Linear Mechanics. By PROF. DR. N. KRYLOFF and PROF. DR. N. BOGOLIUBOFF ..	523
The Raman Spectra of Propylene and Iso-Butane. By R. ANANTHAKRISHNAN	527
The Raman Spectra of Selenious Acid and Its Sodium Salts. By C. S. VENKATESWARAN	533
Resonance Curves for a Quartz Oscillator Immersed in Liquids. By S. PARTHASARATHY	544
Rotational Analysis of the Ångström Bands at $\lambda\lambda$ 6080 and 6620 Å.U. By R. K. ASUNDI	554
On the Dissociation Energy of Carbon Monoxide. By R. K. ASUNDI and R. SAMUEL	562
Dispersion of Depolarisation of Rayleigh Scattering. Part I.—Fatty Acids. By K. S. KRISHNAN	566
On the Structure and Optical Characters of the Nacre in Iridescent Shells.—Part I. By V. S. RAJAGOPALAN	572
The Physical Identity of Enantiomers. Part II. (a) The Rotatory Dispersion of <i>d</i> -, <i>l</i> - & <i>dl</i> -forms of Iso-nitrosocamphor and their Sodium Derivatives. (b) The Differences in the Physiological Action of <i>d</i> -, <i>l</i> - & <i>dl</i> -forms of Sodionitrosocamphor. By BAWA KARTAR SINGH and SHEONATH PRASAD	586
Diffraction of Light by Ultrasonic Waves—Part II. Reflection and Transmission Phenomena. By S. PARTHASARATHY	594
Doppler Effect in Light Scattering in Liquids. Part III.—Polarisation of Light Transversely Scattered by Formic and Acetic Acids. By B. V. RAGHAVENDRA RAO	607

FIRST ANNUAL MEETING OF THE INDIAN ACADEMY OF SCIENCES.

(Held at Bombay on 18th December 1935.)

PRESIDENTIAL ADDRESS.

BY SIR C. V. RAMAN, Kt., F.R.S., N.L.

THE INDIAN ACADEMY OF SCIENCES was registered at Bangalore on the 24th of April 1934, and was formally inaugurated at a public meeting held at the Indian Institute of Science on the 31st July 1934, by Amin-ul-Mulk Sir Mirza M. Ismail, Dewan of Mysore. In the ordinary course of events, the Annual Meeting should have been held in July last. But for various reasons it was felt desirable to postpone it till the cold weather so that it would be possible for the Meeting to be conveniently held at some centre outside Bangalore where our Fellows could assemble. There is a peculiar appropriateness in that the Academy which was inaugurated at Bangalore should hold its first annual meeting at Bombay. It is known to all of you that if Bangalore to-day occupies a significant position in the world of science, it is to no small extent due to the far-sighted generosity of a great and enterprising citizen of Bombay, the late Mr Jamsetjee Nusserwanjee Tata. At a time when the Universities of India were few in number and were purely examining bodies, Mr Tata conceived the idea of creating an Imperial Teaching and Research University for the whole of India which would have aims and ideals approximating to those of such ancient foundations of learning as Oxford and Cambridge. In Mr. Harris's life of Tata, we have an authoritative account of the early history of Mr. Tata's scheme. We read that the two reasons which finally lead to Bangalore being the recipient of his princely benefaction to the cause of learning were firstly, the agreeable climate of Bangalore which he regarded as particularly suitable for a centre of advanced teaching and research, and secondly, the generous offer of the Maharaja of Mysore of half a square mile of land, five lakhs of rupees as a capital grant and an annual subsidy of one lakh of rupees towards the establishment of the Institute at Bangalore. Forty years ago, in this way was forged an intellectual link between Bangalore and Bombay which is now indissoluble and which has had and will, I believe, continue to have a far-reaching influence on the progress of science in India.

The idea of establishing an All-India Academy of Sciences was first clearly put forth in an editorial article in the Journal "Current Science"

published from Bangalore in May 1933. After a period of discussion and consultation with scientific men all over India, the decision to inaugurate the Academy with its provisional headquarters at Bangalore was finally taken in April 1934. I shall, in the course of this address, refer more in detail to the progress which has since been achieved by the Academy and which has amply justified that decision. But even at this early stage, it is appropriate to mention the large part which our friends in Bombay have played in achieving that progress. At the present time, no fewer than thirty-eight of our Fellows are resident in the Bombay Presidency. The election of such a large number to the distinction of the fellowship has been a natural consequence of the remarkable development in recent years of scientific research activities in the Bombay Presidency. I shall have more to say about this later in my address, and it will be sufficient to remark now that the published Proceedings of the Academy bear ample witness to the scientific energy of Dr. T. S. Wheeler and his colleagues at the Royal Institute of Science and to the deep interest taken in the progress of the Academy by the officers of the Meteorological Department at Poona, and the schools of scientific research which have developed at Poona and other parts of the Bombay Presidency. For all these reasons, it is very appropriate that we meet to-day at Bombay. I hope that this gathering will be the first of a series to be held year after year at various centres of scientific research in India. It is desirable that the annual meetings of the Academy should serve to bring together its Fellows from various parts of India at least once a year and thus to strengthen the feeling of scientific comradeship that unites them. Science like other products of human activity, stands to gain immensely from the personal contacts of leading workers. It is earnestly to be hoped that our present meeting will furnish opportunities for such contacts and thus serve to promote the cause of the advancement of science in our great country.

Before I pass to review the work and progress of the Academy since its foundation, I must express the gratitude of the Council to Your Excellency in having consented to grace the occasion to-day and encourage us by your presence here. I must also express the gratitude of the Council to the Fellows of the Academy in Bombay headed by Dr. Wheeler our Vice-President, and to the Reception Committee presided over by you Mr. Vice-Chancellor, who have been at immense pains to organise this our first Annual Meeting on a scale worthy of the occasion.

When the Academy was inaugurated, it commenced its activities with 65 Fellows. The Council obtained permission from the General Body of Fellows to elect fresh Fellows up to a maximum of 200 and also Honorary

Fellows up to a maximum of 30 from amongst the most distinguished scientists of the world. This permission has been acted upon and we have to-day 173 Fellows in India and 30 Honorary Fellows. Our Honorary Fellows include some of the most active and influential scientific men in Europe and America, whose sympathy and co-operation will, I am sure, be of the greatest benefit to the Academy.

The British list of Honorary Fellows includes Lord Rutherford, Sir William Bragg, Sir F. Gowland Hopkins, Sir John Russell, Prof. O. W. Richardson, Prof. Robert Robinson, Prof. A. V. Hill, Prof. P. A. M. Dirac, Prof. A. C. Seward and Prof. G. H. Hardy. The American list includes Prof. R. A. Millikan, Prof. A. H. Compton, Prof. N. L. Bowen, Prof. Harvey Cushing, Prof. D. D. Van Slyke and Prof. G. N. Lewis. The German list includes Prof. A. Sommerfeld, Prof. W. Heisenberg, Prof. Hans Fischer, Prof. H. Wieland and Prof. F. Paschen. From France we have Prof. A. Cotton and Madame Irene Curie-Joliot. From Sweden we have Prof. K. M. G. Siegbahn and Prof. Th. Svedberg. From Denmark and Holland we have respectively Prof. Niels Bohr and Prof. P. Zeeman. From Italy we have Prof. E. Fermi and Prof. S. Belfanti and from Russia Prof. I. P. Pavlov.

It is noteworthy that the list of 30 includes one woman scientist, Madame Irene Curie-Joliot. It must have given our Fellows great pleasure to read the recent announcement of the award of the Nobel Prize in Chemistry to this lady and her husband jointly.

Our list of Fellows in India is representative of every important branch of science. Physics and Meteorology are represented by 31 Fellows, Mathematics and Astronomy by 18, Chemistry by 40, Zoology and Anthropology by 17, Agriculture, Forestry and Botany by 35, Medicine by 15 and Geology by 8. We have only 6 Engineering Fellows but they include some very distinguished names including some very familiar in Bombay, *viz.*, Sir M. Visvesvaraya and Dewan Bahadur N. N. Iyengar. Our list of Fellows is also representative of all parts of India. Bombay heads the list with 38 Fellows, closely followed by the Madras Presidency by 35 and Mysore State by 33. Other provinces are also well represented. We have 21 Fellows in the United Provinces, 13 from the Punjab, 11 from Bengal, 8 from the Central Provinces; Bihar and Orissa, Hyderabad, Travancore and Burma are also represented in our list.

The scientific activities of the Academy may be considered under the three heads:—

Meetings for discussion of research papers.

Symposia on special subjects.

Publication of the Proceedings.

I shall consider the last first because in a country like India separated by great distances, by far the most important service that can be rendered to science by the Academy is the regular issue of a scientific journal of high standing in which scientific papers of its Fellows can find prompt publication. I think it will be generally agreed that the Academy has achieved very gratifying success in this direction. Ever since the formal inauguration of the Academy, the Proceedings have appeared month after month with unbroken regularity on the due date. A very great amount of material has reached the Academy from many quarters. The examination of this material and the selection of suitable papers has naturally been a formidable task. That it has so far been accomplished without any signs of breakdown is largely due to the co-operation which the Academy has been so fortunate to secure. A special word of praise is due to the Superintendent of the Bangalore Press who has maintained a high standard of printing both as regards accuracy and technical finish and has enabled the Journal to appear with unfailing punctuality. To the numerous Fellows who have acted as referees for papers often at great cost of time and trouble, the Council are deeply indebted. A heavy burden has also fallen on the Secretaries and on the Manager of the office which they have discharged with conspicuous devotion and success. I believe our Fellows have by this time learnt to look forward to the appearance of the Proceedings on the first of every month and to peruse its contents with eagerness and satisfaction. The volume of published material has grown so rapidly that commencing from July 1935 it was found necessary to separate the Proceedings into two parts, A, Physical and Mathematical Series, and B, Biological Series respectively. The two numbers of the Journal appearing in each month have each contained roughly 100 pages of printed matter together with a very substantial number of illustrated plates. In view of the volume of published matter, the Council have decided in future to issue two volumes instead of one per annum for each of the two sections of the Proceedings.

I will next refer to the Symposia organised by the Academy. There was one in August 1934 on Molecular Spectra which was attended by 50 Fellows from all over India. The shorter papers submitted for this symposium have all been published in the Proceedings. A very valuable and detailed report by Prof. R. Samuel of the Aligarh University has already been printed and circulated to leading specialists on the subject. A detailed report by Mr. N. S. Nagendra Nath on the subject of Dynamics of Molecular Vibrations is also to be printed and issued shortly together with Dr. Samuel's Report as a special publication. In October 1935,

a symposium on Disease Resistance in Plants was held at Coimbatore. This was largely attended and was a successful gathering, mainly as the result of the efforts of our Coimbatore friends who worked hard to organise the function. At the present meeting in Bombay, a symposium on Colloid Science has also been arranged.

An important part of the regular work of the Academy is the holding of scientific meetings at which papers presented to it are read and discussed. While such meetings are usually held at Bangalore, the Council have also encouraged the idea of meetings being held at other centres for the reading of papers on the occasion of special gatherings such as Symposia and the annual meetings.

A matter of great concern to the Academy is the question of providing money for these activities, especially for the cost of publication of the Proceedings which is very heavy. That it has been possible at all to carry on the work of the Academy without a complete financial breakdown is largely due to the generosity of the external authorities who have come forward to help us. Chief amongst these, I should mention the Government of His Highness the Maharaja of Mysore who have sanctioned a grant of Rs. 3,000 per annum for a period of five years. His Highness the Ruler of Bhopal has been pleased to sanction an annual recurring grant of Rs. 500, and the Government of His Highness the Maharaja of Cochin have also sanctioned an annual recurring grant of Rs. 250. The Imperial Council of Agricultural Research have sanctioned a grant of Rs. 500 per annum for 3 years. The latest benefaction to the Academy is from the Government of His Highness the Maharaja of Travancore of Rs. 1,000 for this year. The Council of the Indian Institute of Science sanctioned a grant of Rs. 2,000 for the current year. The University of Nagpur have given us Rs. 100 and one of our Fellows, Mr. T. W. Barnard, has made a special contribution of Rs. 50.

It must be obvious that the publication of a scientific journal rather, of two scientific journals appearing month after month, is a very expensive proposition. Unless we have an assured income of at least Rs. 25,000 per annum, it will not be possible to carry on this work in a satisfactory manner. Only about one-third of this sum can be found from the regular subscriptions of our Fellows. In these days, the building up of a subscription list for a new scientific periodical is a slow and difficult business. It is here, however, that great assistance can be rendered to us by the educated public in India. If every college, every scientific institution and every department of the local Governments subscribed, as it should, for one copy of the Proceedings of the Academy, our financial problem would be greatly eased. I earnestly appeal to all the other Governments and Universities in India to

come to our aid. Even a modest annual contribution from each of them would aggregate to a total sum which would enable the Academy to go forward in its great task without fear of financial breakdown.

I think it would be not inopportune to consider at this stage the nature of the services which the Academy can render to science in India. We live in an era of scientific progress and it is a very gratifying feature that India is beginning to pull its weight in this respect. Modern scientific progress shows side by side two apparently contradictory features. On the one hand, we have an enormous accumulation of raw scientific material, the significance of which, in many cases, is hardly apparent except to specialists in very limited fields of investigation. On the other hand, we have a great process of scientific synthesis going on tending towards the simplification and unification of the fundamental principles of natural knowledge in all its ramifications. It should never be overlooked that science is in reality a great impartible estate and that the boundaries drawn across it to divide it into restricted fields are in essence artificial. I think the history of science has shown over and over again that it is only by boldly cutting across these artificial boundaries that progress of real significance can be achieved. It is precisely this feature that lends importance to the activities of such an Academy as ours where men of science of widely different scientific interests come together in a common endeavour and seek to understand each other's points of view. While specialisation is necessary, an excessively narrow outlook defeats the primary purpose of science which is to advance our essential comprehension of nature as a whole. It is, therefore, one of the most important functions of our Academy to promote co-operation between men who profess knowledge of different branches of science. This is effected in various ways. In the Proceedings of the Academy the Fellows and indeed all scientific men have an opportunity of obtaining at least a general idea of what is being done in India in fields of knowledge other than their own speciality. In the scientific meetings of the Academy and especially in the Symposia, they have a valuable opportunity of discussing problems of common interest from different points of view.

I will also say a word about the Academy in relation to the nation at large. It is inevitable that the Academy, consisting as it does of the most active workers in the country who are representatives of the different parts of India and of different branches of science, will soon come to be regarded as the most authoritative body to speak in the name of India on all matters touching the progress of science. The potentialities of such an Academy in the way of national service are almost unlimited. What it can actually

achieve depends on the measure of support and recognition that it receives from the Governments of India and from the general public. I do not think that any calls for service from responsible quarters will find us unwilling or unprepared

According to the Memorandum of Association, the headquarters of the Academy has been fixed at Bangalore for a period of three years in the first instance. I have no doubt it is the general feeling of all our Fellows that this location has fully justified itself. In this connection, I should mention the generous personal gift by His Highness the Maharaja of Mysore of ten acres of land in the vicinity of the Indian Institute of Science as a permanent location for the Academy. The location selected is a historic spot close to one of the four towers set up by Kempe Gowda, a former Hindu ruler, as a limit for the extension of his city. A relief map shows this site to be the highest spot in Bangalore. Indeed, standing on it at ground-level we see a magnificent panorama stretching out towards the horizon in all directions with Nandidroog in the blue distance towards the north, Sankey's Reservoir and the City of Bangalore to the south, the Palace Gardens to the east and the Indian Institute of Science to the west with the Sivaganga hills looming in the distance. Such a spot is indeed a worthy site for the location of an Academy of Sciences intended to play a great part in the intellectual life of the nation. Such a site also demands a noble edifice which would catch the eye and strike the imagination of both the present and future generations. Has not Bombay some far-sighted and philanthropic donor who would come forward to build an Academy of Sciences for all India and thus immortalize himself and find a place in the memory of India side by side with Jamsetji Tata. The permanent location at Bangalore of an Academy of Sciences would indeed be a fitting completion of Tata's great work. The Academy would serve as a link between the Institute and the outer world of science, each strengthening the other and helping it to reach the full fruition of its aims.

UNITARY THEORY OF FIELD AND MATTER.

I. Classical Treatment. Charged Particle with Magnetic Rest-Moment.

BY MAX BORN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received December 3, 1935.

(Communicated by Sir C V Raman, Kt, FRS, NL)

Introduction.

THE principal problem of a unitary theory of field and matter is the derivation of the equations of motion of a singularity representing a particle. Several attempts have been made¹ in this direction but none is quite satisfactory. I shall give here a new derivation of the equations of motion of a spinning particle on the basis of the classical treatment of the field equations. This derivation is simple and absolutely rigorous under the suppositions which have to be made so as to give the problem a definite meaning. The chief assumption can be expressed in the usual language of Maxwell's theory in this way: the external field must be constant over the "diameter" of the particle. The unitary field theory does not distinguish between external and internal field, the corresponding supposition is: the (total) field approaches a constant field at a great distance from the singularity. We shall start from a variation principle representing both the motion of the field and of the singularity. Correspondingly it consists of two parts, a space-time integral and a pure time integral. But we shall write the latter also as space-time integral making use of Dirac's δ -function. In this way a great clearness about the physical interpretation of the equations is reached; but the mathematical laws can be easily expressed without symbolic functions and this will be done throughout.

This method leads in the most natural way to the introduction of the spin in the classical theory. Kramers² has first shown that a classical spin theory is possible, indeed, and that the quantization of it leads to Dirac's wave equation. The spinning particle is considered by Kramers as a mass point connected with an angular momentum the motion of which is

¹ M. Born and L. Infeld, *Proc. Roy. Soc.*, 1934, A 144, 425; E. Feenberg, *Phys. Rev.*, 1935, 47, 148; T. Frenkel, *Proc. Roy. Soc.*, 1934, A 416, 930.

² H. A. Kramers, *Physica*, 1934, 1, 825; Zeeman, *Verhandelingen*, 1935, p. 403.

described by relativistically invariant formulæ. We show how Kramers' formulæ can be derived from the unitary field theory.

The problem of quantization shall be treated later.

1. Variation principle and field equations.³

The Lagrangian $L(f_{kl})$ of the field is supposed to be invariant for Lorentz transformation; but we do not assume a special function and rely only on the fact proved in previous publications that there exists such a function for which the energy and momentum of a point charge are finite.

To this Lagrangian of the field we add a Lagrangian of the singularity which we suppose to have the form $l(\phi_k, f_{kl})\delta$, where δ is a symbolic function of the type introduced by Dirac. We assume that in the coordinate system where the singularity is at rest, $\delta(x, y, z) = 0$ at every point except in the singularity x_0, y_0, z_0 , where δ is infinite in such a way that

$$\int \delta dv = 1, \quad dv = dx dy dz.$$

The assumption that l depends explicitly on the potentials ϕ_k does not lead to any difficulties as in the theory of Mie⁴. He introduced the ϕ_k in the Lagrangian of the field: $L(\phi_k, f_{kl})$; this leads to contradictions to the fact that the absolute value of the potential in free space has no physical meaning. As the absolute value of the potential in the singularity has a definite meaning, the introduction of the ϕ_k in the Lagrangian of the singularity is permitted.

The variation principle governing field and matter is

$$(1, 1) \quad \int \{L(f_{kl}) + l(\phi_k, f_{kl})\delta\} dv dt = \text{Extremum}.$$

We define the second kind of field components in the usual way by

$$(1, 2) \quad p^{kl} = \frac{\partial L}{\partial f_{kl}};$$

further we put

$$(1, 3) \quad \rho^k = \frac{\partial l}{\partial \phi_k}, \quad m^{kl} = \frac{\partial l}{\partial f_{kl}}.$$

As the f_{kl} are connected with the potentials ϕ_k by

$$(1, 4) \quad f_{kl} = \frac{\partial \phi_k}{\partial x^l} - \frac{\partial \phi_l}{\partial x^k},$$

one has the identities

$$(1, 5) \quad \frac{\partial f^{*kl}}{\partial x^l} = 0, \quad \text{or} \quad \frac{\partial f_{kl}}{\partial x^m} + \frac{\partial f_{lm}}{\partial x^k} + \frac{\partial f_{mk}}{\partial x^l} = 0,$$

³ The notations are those used in the previous papers of Born and Infeld, cited above.

⁴ G. Mie, *Ann. d. Phys.*, **37**, p. 511; **39**, p. 1; **40**, p. 1.

where f^{*kl} is the dual tensor to f_{kl} ; (1, 5) is the first set of field equations. The second set are the Eulerian equations of the variation principle:

$$(1, 6) \quad \frac{\partial p^{kl}}{\partial x^l} = \rho^k \delta - \frac{\partial m^{kl} \delta}{\partial x^l}.$$

From this follows the continuity equation

$$(1, 7) \quad \frac{\partial \rho^k \delta}{\partial x^k} = 0.$$

We introduce now the space-vector notation⁵ (with $c = 1$):

$$(1, 8) \quad \left\{ \begin{array}{l} (\phi^1, \phi^2, \phi^3, \phi^4) = (\vec{A}, \phi), \\ (f_{23}, f_{31}, f_{12}) = \vec{B}, (f_{14}, f_{24}, f_{34}) = \vec{E}, \\ (p_{23}, p_{31}, p_{12}) = \vec{H}, (p_{14}, p_{24}, p_{34}) = \vec{D}, \\ (\rho^1, \rho^2, \rho^3, \rho^4) = (e \vec{v}, e), \\ (m_{23}, m_{31}, m_{12}) = \vec{m}, (m_{14}, m_{24}, m_{34}) = \vec{p}, \end{array} \right.$$

Then the field equations (1, 5), (1, 6) are

$$(1, 9) \quad \left\{ \begin{array}{l} \text{rot } \vec{H} - \dot{\vec{D}} = \delta(e \vec{v} + \vec{p}) - \text{rot } (\vec{m} \delta), \\ \text{div } \vec{D} = \delta e - \text{div } (\vec{p} \delta), \\ \text{rot } \vec{E} + \dot{\vec{B}} = 0, \\ \text{div } \vec{B} = 0, \end{array} \right.$$

and the equation of continuity (1, 7)

$$(1, 10) \quad \frac{\partial e \delta}{\partial t} + \text{div } (e \vec{v} \delta) = 0$$

The vectors \vec{p}, \vec{m} have obviously to be interpreted as an *electric and magnetic moment*, connected with the singularity

We assume that in the coordinate system, where the particle is at rest, there is only a magnetic moment (spin) \vec{m} .

Then

$$(1, 11) \quad \vec{p} = -(\vec{v} \times \vec{m}).$$

The invariance of the variation principle for Lorentz transformation implies the two identities

⁵Pulling up and down of the indices 1, 2, 3 changes the sign; that of the index 4 does not. For instance:

$$(\rho_1, \rho_2, \rho_3, \rho_4) = (-e \vec{v}, e).$$

$$(1, 12) \quad \begin{cases} \vec{E} \times \vec{H} = \vec{D} \times \vec{B}, \\ \vec{E} \times \vec{D} = -\vec{H} \times \vec{B}, \end{cases}$$

which express that I , depends only on the invariants

$$\vec{B}^2 - \vec{E}^2, \quad \vec{E} \cdot \vec{B}.$$

For the line integral we have to suppose invariance as well; this leads to the identities

$$(1, 13) \quad \begin{cases} (\vec{E} \times \vec{m})_0 = (\vec{p} \times \vec{B})_0, \\ (\vec{E} \times \vec{p})_0 = -(\vec{m} \times \vec{B})_0, \end{cases}$$

where the index 0 indicates that the co-ordinates of the singularity have to be substituted.

In the rest-system, where $\vec{v} = 0$, $\vec{p} = 0$, one has

$$(1, 14) \quad \begin{cases} (\vec{E} \times \vec{m})_0 = 0, & (\vec{p} \times \vec{B})_0 = 0, \\ (\vec{E} \times \vec{p})_0 = 0, & (\vec{m} \times \vec{B})_0 = 0 \end{cases} \quad \left\{ \begin{array}{l} v = 0 \end{array} \right.$$

If any quantity F vanishes at the singularity one has

$$\left[\frac{dF}{dt} \right]_0 = \left[\vec{v} \cdot \text{grad } F + \frac{\partial F}{\partial t} \right]_0 = 0,$$

therefore in the rest system

$$(1, 15) \quad \left(\frac{\partial F}{\partial t} \right)_0 = 0, \text{ for } v = 0, \text{ if } (F(v))_0 = 0$$

Applying this to (1, 13) we get

$$(1, 16) \quad \begin{cases} \left[\frac{\partial}{\partial t} (\vec{E} \times \vec{m}) - \frac{\partial}{\partial t} (\vec{p} \times \vec{B}) \right]_0 = 0, \\ \left[\frac{\partial}{\partial t} (\vec{E} \times \vec{p}) + \frac{\partial}{\partial t} (\vec{m} \times \vec{B}) \right]_0 = 0. \end{cases}$$

2. Boundary conditions at the singularities.

The equations (1, 9) are equivalent to the postulate, that the corresponding homogeneous equations

$$(2, 1) \quad \begin{cases} \text{rot } \vec{H} - \dot{\vec{D}} = 0, & \text{rot } \vec{E} + \dot{\vec{B}} = 0, \\ \text{div } \vec{D} = 0, & \text{div } \vec{B} = 0 \end{cases}$$

hold at any point except at the singularity where certain boundary conditions have to be fulfilled. These are found by integrating the differential equations (1, 9) directly, and after multiplying them by x, y, z , over a small

sphere. The essence of the unitary theory of matter and field consists in the assumption that all volume integrals of the types

$$\int_0 D_r dv, \int_0 D_x y dv, \int_0 \dot{D}_x dv, \int_0 \dot{D}_x y dv, \dots$$

vanish if the radius of the sphere is contracting to zero, even if the sphere contains a singularity. But the volume integrals of space derivatives (rot, div) can be transformed into surface integrals, which tend to finite values. In the rest-system of the singularity we get easily from (1,9), (1, 10):

$$(2, 2) \quad \epsilon = 0,$$

$$(2, 3) \quad \left\{ \begin{array}{l} \int_0 (\vec{n} \times \vec{H}) d\sigma = 0, \quad \int_0 \vec{n} \cdot \vec{D} d\sigma = e, \\ \int_0 (\vec{n} \times \vec{E}) d\sigma = 0, \quad \int_0 \vec{n} \cdot \vec{B} d\sigma = 0; \end{array} \right.$$

$$(2, 4) \quad \left\{ \begin{array}{l} \int_0 x (\vec{n} \times \vec{H})_x d\sigma = 0, \dots\dots\dots \\ \int_0 y (\vec{n} \times \vec{H})_x d\sigma = m_x, \dots\dots\dots \\ \int_0 z (\vec{n} \times \vec{H})_x d\sigma = -m_y, \dots\dots\dots \end{array} \right.$$

$$(2, 5) \quad \int_0 \vec{r} (\vec{n} \cdot \vec{D}) d\sigma = e \vec{r}_0,$$

$$(2, 6) \quad \left\{ \begin{array}{l} \int_0 x (\vec{n} \times \vec{E})_x d\sigma = 0, \dots\dots\dots \\ \int_0 y (\vec{n} \times \vec{E})_x d\sigma = 0, \dots\dots\dots \\ \int_0 z (\vec{n} \times \vec{E})_x d\sigma = 0, \dots\dots\dots \end{array} \right.$$

$$(2, 7) \quad \int_0 \vec{r} (\vec{n} \cdot \vec{B}) d\sigma = 0.$$

Here \vec{n} is the unit vector normal to the surface element $d\sigma$ of the sphere surrounding the singularity.

3. Dynamical boundary conditions at the singularity.

To make full use of the variation principle (1, 1) we have not only to vary the field for a given motion of the singularity, but also to vary this motion, *i.e.*, the functions, $\vec{r}_0(t)$, $\vec{m}(t)$ for a given field. This variation influences only the Lagrangian l of the singularity. Now we can assume that l has the form

$$(3, 1) \quad l = \rho^k \phi_k + \frac{1}{2} m^{kl} f_{kl} = e(\phi - \vec{v} \cdot \vec{A}) + \vec{m} \cdot \vec{B} - \vec{p} \cdot \vec{E},$$

since this gives the same field equation (1, 9).

Here ϕ , \vec{A} , \vec{B} , \vec{E} are to be considered as functions of $\vec{r}_0(t)$, whereas $\vec{v} = \dot{\vec{r}}_0(t)$, $\vec{p} = \vec{m}(t) \times \dot{\vec{r}}_0(t)$.

If ϕ , \vec{A} , \vec{B} , \vec{E} were continuous functions of their arguments, one could apply directly the formal rules of the calculus of variations on the integral $\int l dt$. But in fact these functions are just supposed to have a singular point at \vec{r}_0 , and the assumption, that the spatial derivatives exist, is not justified. Therefore we have to make the variation in a more elaborate way.

We replace $e\delta$, $e \vec{v} \delta$ by a little more general δ -functions, ρ , $\rho \vec{v}$; these are first considered as continuous distributions of density and current around the world line which has to become the representation of the moving singularity. We introduce instead of x, y, z, t , the parameters ξ, η, ζ, τ , where τ is the proper time for each world line in the continuous current ρ , $\rho \vec{v}$, given by a special set of values of the parameters ξ, η, ζ . Then the variation principle can be written

$$(3, 2) \quad \int d\tau \left(\int \int \int d\xi d\eta d\zeta \left\{ \dot{\tau} (\rho_0 \phi + \vec{m} \cdot \vec{B}) - \dot{\tau}_0 (\rho_0 \vec{A} - (\vec{m} \times \vec{E})) \right\} \right) = \text{Extr.},$$

where $\rho_0(\xi, \eta, \zeta)$ is the rest density, and $\dot{\tau}_0(\xi, \eta, \zeta, \tau)$, $\dot{\tau}(\xi, \eta, \zeta, \tau)$ are the unknown functions; the point indicates the derivative with respect to τ .

We assume that the functions ϕ , \vec{A} , \vec{B} , \vec{E} are continuously depending on their arguments x_0, y_0, z_0, t_0 , and that their singularities appear only when the continuous current is contracted to a world line. We shall show that these singularities have no influence on the differential equation of the extremal curve.

We have to add the condition expressing τ being the proper time :

$$(3, 3) \quad \dot{t}_0^2 - \dot{x}_0^2 - \dot{y}_0^2 - \dot{z}_0^2 = 1.$$

The variation principle (3, 2) is a generalisation of the well-known principle giving Lorentz equations of motion:

$$\int d\tau \left(\int d\xi d\eta d\zeta \cdot \rho_0 (\dot{t}_0 \phi - \dot{\vec{r}}_0 \cdot \vec{A}) \right) = \text{Extr},$$

and can be treated in exactly the same way. We take account of the subsidiary condition (3, 3) by a Lagrangian multiplier $\mu(\xi, \eta, \zeta, \tau)$, then we get

$$(3, 4) \quad \begin{cases} \iiint d\xi d\eta d\zeta \left(\frac{d\mu}{d\tau} \dot{\vec{r}}_0 - \vec{K} \right) = 0, \\ \iiint d\xi d\eta d\zeta \left(\frac{d\mu}{d\tau} \dot{t}_0 - \kappa \right) = 0, \end{cases}$$

where

$$(3, 5) \quad \begin{cases} \vec{K} = \dot{t}_0 (\rho_0 \vec{E} - \text{grad } (\vec{m} \cdot \vec{B})) + \rho_0 (\dot{\vec{r}}_0 \times \vec{B}) + \frac{d}{dt} (\vec{m} \times \vec{E}) \\ \quad - [\dot{\vec{r}}_0 \times \text{rot } (\vec{m} \times \vec{E})], \\ \kappa = (\rho_0 \dot{\vec{r}}_0 \cdot \vec{E}) + \dot{\vec{r}}_0 \left[\frac{d}{dt} (\vec{m} \times \vec{E}) - \text{grad } (\vec{m} \cdot \vec{B}) \right] \end{cases}$$

Now we can make the limiting process of contracting the current to a world line. Since the space ξ, η, ζ is normal to this line, we can transform it to rest; then $\dot{\vec{r}}_0 = 0$, $\dot{t}_0 = 1$, and we get

$$(3, 6) \quad \left\{ \begin{aligned} \left\{ \frac{d\mu}{dt} \vec{v} - e \vec{E} + \text{grad } (\vec{m} \cdot \vec{B}) - \frac{d}{dt} (\vec{m} \times \vec{E}) \right\}_0 &= 0, \\ \left\{ \frac{d\mu}{dt} \right\}_0 &= 0 \end{aligned} \right\}_{v=0}.$$

Besides these equations we get another one by varying \vec{m} in (3, 2); this gives obviously

$$(3, 7) \quad (\vec{B} - [\vec{v} \times \vec{E}])_0 = 0,$$

and in the rest-system:

$$(3, 8) \quad \vec{B}_0 = 0 \quad \text{for } \vec{v} = 0.$$

The multiplier μ plays the rôle of a (constant) mass, concentrated in a point. The assumption of a point mass is consistent with the mathematical formalism, but in contradiction to the idea of the unitary field theory.

We take therefore

$$(3, 9) \quad \mu = 0$$

and have the *dynamical boundary conditions* :

$$(3, 10) \quad \vec{K}^0 = \left[e\vec{E} - \text{grad} (\vec{m} \cdot \vec{B}) + \frac{d}{dt} (\vec{m} \times \vec{E}) \right]_0 = 0.$$

From (3, 7) and (1, 11) it follows that

$$(3, 11) \quad (\vec{m} \cdot \vec{B} - \vec{p} \cdot \vec{E})_0 = 0.$$

Corresponding to the remark at the end of section 1, there is also

$$(3, 12) \quad \left[\frac{d}{dt} (\vec{m} \cdot \vec{B}) \right]_0 = \left[\frac{d}{dt} (\vec{p} \cdot \vec{E}) \right]_0 = 0 \quad \text{for } \vec{v} = 0.$$

4 Conservation laws.

We multiply (1, 5) by $p^{ln} + \delta m^{ln}$ and sum over l, n :

$$\frac{\partial I_l}{\partial x^k} + \frac{\partial}{\partial x^l} (p^{ln} f_{nk}) = f_{nk} \frac{\partial p^{nl}}{\partial x^l} - \delta \left(\frac{1}{2} m^{ln} \frac{\partial f_{ln}}{\partial x^k} + m^{ln} \frac{\partial f_{nk}}{\partial x^l} \right).$$

With help of (1, 6) we get :

$$(4, 1) \quad \frac{\partial}{\partial x^l} (L \delta_{kl} - p^{nl} f_{nk}) = \delta \left(f_{kn} p^n - \frac{1}{2} m^{ln} \frac{\partial f_{ln}}{\partial x^k} \right) + \frac{\partial}{\partial x^l} (m^{ln} f_{kn} \delta)$$

We define the energy-momentum tensor

$$(4, 2) \quad T_{kl} = L \delta_{kl} - p^{ln} f_{kn},$$

and the corresponding tensor

$$(4, 3) \quad t_{kl} = \lambda \delta_{kl} - m^{ln} f_{kn}$$

where

$$(4, 4) \quad \lambda = \frac{1}{2} m^{nl} f_{nl}.$$

Then (4, 1) becomes .

$$(4, 5) \quad \frac{\partial T_{kl}}{\partial x^l} = \delta f_{kn} p^n + \frac{1}{2} f_{nl} \frac{\partial (m^{nl} \delta)}{\partial x^k} - \frac{\partial (t_{kl} \delta)}{\partial x^l}.$$

Now we go over to the space-vector notation :

$$(4, 6) \quad (T_{kl}) = \begin{Bmatrix} X_x & X_y & X_z & S_x \\ Y_x & Y_y & Y_z & S_y \\ Z_x & Z_y & Z_z & S_z \\ S_x & S_y & S_z & U \end{Bmatrix},$$

where Maxwell's tensions

$$(4, 7) \quad \begin{cases} X_x = -H_y B_y - H_z B_z + D_x E_x + L, \dots\dots\dots \\ X_y = Y_x = -H_y B_x + D_x E_y = -H_x B_y + D_y E_x, \dots \end{cases}$$

the Poynting vector

$$(4, 8) \quad \vec{S} = \vec{E} \times \vec{H} = \vec{D} \times \vec{B},$$

the energy density

$$(4, 9) \quad U = \vec{E} \cdot \vec{D} + L;$$

and correspondingly

$$(4, 10) \quad \lambda = (\vec{m} \cdot \vec{B} - \vec{p} \cdot \vec{E})_0,$$

$$(4, 11) \quad t_{k'} = \begin{Bmatrix} x_x & x_y & x_z & s_x \\ y_x & y_y & y_z & s_y \\ z_x & z_y & z_z & s_z \\ s_x & s_y & s_z & u \end{Bmatrix}$$

This tensor is symmetric on account of (1, 13) and (3, 11) :

$$(4, 12) \quad \begin{cases} x_x = (-p_y E_y - p_z E_z + m_z B_x)_0 = (-m_y B_y - m_z B_z + p_x E_x)_0, \dots \\ x_y = y_x = (-m_y B_x + p_x E_y)_0 = (-m_x B_y + p_y E_x)_0, \dots \\ \vec{s} = (\vec{E} \times \vec{m})_0 = -(\vec{B} \times \vec{p})_0, \\ u = (\vec{m} \cdot \vec{B})_0 = (\vec{p} \cdot \vec{E})_0. \end{cases}$$

In consequence of (1, 11) and (3, 8) all these quantities vanish in the rest-system :

$$(4, 13) \quad \left\{ \begin{array}{l} \lambda = 0 \\ x_x = 0, \dots, x_y = y_x = 0, \dots \\ \vec{s} = 0 \\ u = 0 \end{array} \right\} \text{ for } \vec{v} = 0.$$

We write now (4, 5) for the rest-system :

$$(4, 14) \quad \begin{cases} \frac{\partial S_x}{\partial t} + \text{div } \vec{X} = e E_x + \vec{B} \cdot \frac{\partial \vec{m}}{\partial x} - \vec{E} \cdot \frac{\partial \vec{p}}{\partial x} - \delta \dot{s}_x - \text{div } (\vec{x} \delta), \\ \text{---} \text{---} \text{---} \text{---} \text{---} \\ \frac{\partial U}{\partial t} + \text{div } \vec{S} = \delta (\vec{B} \cdot \dot{\vec{m}} - \vec{E} \cdot \dot{\vec{p}}) - \delta \dot{u} - \text{div } (\vec{s} \delta). \end{cases}$$

We integrate over a small sphere surrounding the singularity :

$$\begin{aligned} \int_0 (\vec{X} \cdot \vec{n}) d\sigma &= \left[e E_x - \vec{m} \cdot \frac{\partial \vec{B}}{\partial x} + \frac{d}{dt} (\vec{m} \times \vec{E})_x \right]_0 = K_x^0, \\ \text{---} \text{---} \text{---} \text{---} \text{---} \\ \int_0 (\vec{S} \cdot \vec{n}) d\sigma &= 0; \end{aligned}$$

here we have made use of the remark at the end of the last section of putting equal to zero the time derivatives of all quantities which vanish in the rest-system.

Comparing this with (3, 6) we find

$$(4, 15) \quad \begin{cases} \int_0 \vec{X} \cdot \vec{n} \, d\sigma = 0, \dots \\ \int_0 \vec{S} \cdot \vec{n} \, d\sigma = 0. \end{cases}$$

Now we multiply the third equation (4, 14) with y , the second with z , subtract and integrate, then we find in exactly the same way

$$(4, 16) \quad \int_0 (\vec{N}_x \cdot \vec{n}) \, d\sigma = (\vec{r}_0 \times \vec{K}^0)_x = 0,$$

where

$$(4, 17) \quad \vec{N}_x = (yZ_z - zY_z, \quad yZ_y - zY_y, \quad yZ_x - zY_x), \dots$$

The operation applied to (4, 14) which leads to (4, 16) must be completed by multiplying the first equation by t , the last by x , and integrating; then it represents a 6-vector (antisymmetrical tensor). But since t is constant with respect to the integration, the term with t vanishes in consequence of (4, 15), and we have

$$\begin{aligned} \int_0 (x \frac{\partial U}{\partial t} + x \operatorname{div} \vec{S}) \, dv &= x_0 (\vec{B} \cdot \dot{\vec{m}} - \vec{E} \cdot \dot{\vec{p}} - \dot{u})_0 \\ &= -x_0 (\dot{\vec{m}} \cdot \vec{B} - \dot{\vec{p}} \cdot \vec{E})_0. \end{aligned}$$

In the rest-system, according to (3, 12), $\left[\frac{d}{dt} (\vec{m} \cdot \vec{B}) \right]_0 = 0$ or, since $\vec{B}_0 = 0$, for $\vec{v} = 0$, $(\dot{\vec{m}} \cdot \vec{B})_0 = 0$, for $\vec{v} = 0$, therefore the right hand term vanishes. We get

$$(4, 18) \quad \int_0 \vec{r} (\vec{S} \cdot \vec{n}) \, d\sigma = 0,$$

as the complement of (4, 16) to a 6-vector equation.

We can now replace the equations (4, 14) containing δ -functions by the postulate, that

$$(4, 19) \quad \begin{cases} \frac{\partial \vec{S}_x}{\partial t} + \operatorname{div} \vec{X} = 0, \dots \\ \frac{\partial U}{\partial t} + \operatorname{div} \vec{S} = 0 \end{cases}$$

holds for all fields satisfying the dynamical boundary conditions (4, 15) and (4, 18) {(4, 16) being a consequence of (4, 15)}.

5 Equations of motion in a constant field.

We define the *total energy and momentum*

$$(5, 1) \quad E = \int U dv, \quad \vec{G} = \int \vec{S} dv,$$

the *centre of energy* \vec{q}

$$(5, 2) \quad E \vec{q} = \int \vec{r} U dv,$$

the *total angular momentum*

$$(5, 3) \quad \vec{M} = \int (\vec{r} \times \vec{S}) dv.$$

We integrate (4, 19) over the whole space, after excluding the singularity by a little sphere; then we do the same after having multiplied the third equation by y , the second by z and subtracting them; at last we do the same after having multiplied the last equation by x . In consequence of the dynamical boundary conditions the integrals over the little sphere vanish, and we get:

$$(5, 4) \quad \left\{ \begin{array}{l} \dot{G}_x + \int_{\infty} (\vec{X} \cdot \vec{n}) d\sigma = 0, \dots \\ \dot{E} + \int_{\infty} (\vec{S} \cdot \vec{n}) d\sigma = 0, \end{array} \right.$$

$$(5, 5) \quad \left\{ \begin{array}{l} \dot{M}_x + \int_{\infty} (\vec{N}_x \cdot \vec{n}) d\sigma = 0, \dots \\ \frac{d}{dt} (E \vec{q}) - \vec{G} + \int \vec{r} (\vec{S} \cdot \vec{n}) d\sigma = 0. \end{array} \right.$$

We shall now consider the case where the field in infinity tends to a constant field E^e, B^e (independent of co-ordinates and time). We represent the total field by

$$(5, 6) \quad \vec{E} = \vec{E}^e + \vec{E}', \quad \vec{B} = \vec{B}^e + \vec{B}',$$

then \vec{E}' and \vec{B}' tend to zero at infinity.

$$(5, 7) \quad \lim_{\infty} \vec{E}' = 0; \quad \lim_{\infty} \vec{B}' = 0.$$

We define the constants

$$(5, 8) \quad \vec{D}^e = - \left(\frac{\partial L}{\partial \vec{E}} \right)_{\substack{\vec{E} = \vec{E}^e, \\ \vec{B} = \vec{B}^e}}, \quad \vec{H}^e = \left(\frac{\partial L}{\partial \vec{B}} \right)_{\substack{\vec{E} = \vec{E}^e, \\ \vec{B} = \vec{B}^e}},$$

and split the total field \vec{D}, \vec{H} into \vec{D}^c, \vec{H}^c and a variable part, which may be denoted by \vec{D}', \vec{H}' .

$$(5, 9) \quad \vec{D} = \vec{D}^c + \vec{D}', \quad \vec{H} = \vec{H}^c + \vec{H}';$$

then \vec{D}', \vec{H}' depend not only on \vec{E}', \vec{B}' , but also on \vec{E}^c, \vec{B}^c , but we have in any case

$$(5, 10) \quad \lim_{\infty} \vec{D}' = 0, \quad \lim_{\infty} \vec{B}' = 0$$

The field $\vec{E}', \vec{B}', \vec{D}', \vec{H}'$ satisfies not only Maxwell's equations in the form (2, 1), but also the boundary conditions (2, 2), \dots (2, 7), since a constant field reduces all the surface integrals to zero.

For the Poynting vector we use first $\vec{S} = \vec{D} \times \vec{B}$, replacing here the vectors \vec{D}, \vec{B} by the sums $\vec{D}^c + \vec{D}', \vec{B}^c + \vec{B}'$, we have

$$\vec{S} = \vec{S}^c + (\vec{D}^c \times \vec{B}') + (\vec{D}' \times \vec{B}^c) + \vec{S}'$$

where $\vec{S}' = \vec{D}' \times \vec{B}'$ and \vec{S}^c a constant, which can be omitted since it does not contribute to (4, 19). We have therefore

$$(5, 11) \quad \vec{G} = \vec{G}^c + (\vec{D}^c \times \int \vec{B}' dv) + (\vec{B}^c \times \int \vec{D}' dv)$$

In the same way we get

$$(5, 12) \quad M_x = M_x^c + D_x^c \int (\vec{r} \cdot \vec{B}') dv - \vec{D}^c \cdot \int \vec{r} B_x' dv \\ - B_x^c \int (\vec{r} \cdot \vec{D}') dv + \vec{B}^c \cdot \int \vec{r} D_x' dv, \dots$$

The energy cannot be split in the same way as it is not a quadratic expression.

We consider now the surface integrals in (5, 4), (5, 5). Here we can develop the integrands with respect to \vec{E}', \vec{B}' or \vec{D}', \vec{H}' , as on a very distant surface they are small compared with the external field, however this may be chosen [equations (5, 7), (5, 10)].

The vector \vec{X} with the components X_x, X_y, X_z is given by (4, 7) with help of I_i ; if we introduce instead the energy density U by (4, 9), for which as a function of \vec{D}, \vec{B} one has

$$(5, 13) \quad \vec{E} = \frac{\partial U}{\partial \vec{D}}, \quad \vec{H} = \frac{\partial U}{\partial \vec{B}},$$

and make use of (4, 7), we have

$$(5, 14) \quad \begin{cases} X_x = -H_y B_y - H_z B_z - D_y E_y - D_z E_z + U, \\ X_y = -H_x B_y + E_x D_y, \\ X_z = -H_x B_z + E_x D_z. \end{cases}$$

Introducing here (5, 6), (5, 9) and neglecting the terms of the second order, we get easily

$$(5, 15) \quad \begin{aligned} \vec{X} \cdot \vec{n} &= \vec{X}^e \cdot \vec{n} + H_x^e (\vec{B}^i \cdot \vec{n}) + E_x^e (\vec{D}^i \cdot \vec{n}) \\ &\quad - [\vec{B}^e \times (\vec{n} \times \vec{H}^i)]_x - [\vec{D}^e \times (\vec{n} \times \vec{E}^i)]_x. \end{aligned}$$

For \vec{S} we use the expression $\vec{E} \times \vec{H}$ and get

$$(5, 16) \quad \vec{S} \cdot \vec{n} = (\vec{S}^e \cdot \vec{n}) - \vec{E}^e (\vec{n} \times \vec{H}^i) + \vec{H}^e (\vec{n} \times \vec{E}^i).$$

A similar, a little lengthy, calculation leads to

$$(5, 17) \quad \begin{aligned} \vec{N}_x \cdot \vec{n} &= (\vec{N}_x^e \cdot \vec{n}) + \vec{B}^e \cdot \int \vec{r} (\vec{n} \times \vec{H}^i)_x d\sigma - B_x^e \int \vec{r} \cdot (\vec{n} \times \vec{H}^i) d\sigma \\ &\quad + \vec{D}^e \cdot \int \vec{r} (\vec{n} \times \vec{E}^i)_x d\sigma - D_x^e \int \vec{r} \cdot (\vec{n} \times \vec{E}^i) d\sigma \\ &\quad - [\vec{H}^e \times \int \vec{r} (\vec{n} \cdot \vec{B}^i) d\sigma]_x - [\vec{E}^e \times \int \vec{r} (\vec{n} \cdot \vec{D}^i) d\sigma]_x. \end{aligned}$$

Now we integrate Maxwell's equation (2, 1) over the whole space except a little sphere around the singularity; the surface integrals over this sphere are given by (2, 3), ... (2, 7), with opposite signs (because of the reversed direction of the outer normal). So we have

$$(5, 18) \quad \begin{cases} \int_{\infty} (\vec{n} \times \vec{H}^i) d\sigma = \int \dot{\vec{D}}^i dv, & \int_{\infty} (\vec{n} \cdot \vec{D}^i) d\sigma = -e \\ \int_{\infty} (\vec{n} \times \vec{E}^i) d\sigma = - \int \dot{\vec{B}}^i dv, & \int_{\infty} (\vec{n} \cdot \vec{B}^i) d\sigma = 0; \end{cases}$$

$$(5, 19) \quad \begin{cases} \int_{\infty} x (\vec{n} \times \vec{H}^i)_x d\sigma = \int x \dot{D}_x^i dv, \dots \\ \int_{\infty} y (\vec{n} \times \vec{H}^i)_x d\sigma = \int (y \dot{D}_x^i + H_z^i) dv - m_z, \dots \\ \int_{\infty} z (\vec{n} \times \vec{H}^i)_x d\sigma = \int (z \dot{D}_x^i - H_y^i) dv + m_y, \dots \end{cases}$$

$$(5, 20) \quad \int_{\infty} \vec{r} (\vec{n} \cdot \vec{D}^i) d\sigma = \int \dot{\vec{D}}^i dv - e \vec{r}_0,$$

$$(5, 21) \quad \begin{cases} \int_{\infty} x (\vec{n} \times \vec{E}')_x d\sigma = - \int x \dot{B}_x' dv, \dots \\ \int_{\infty} y (\vec{n} \times \vec{E}')_x d\sigma = - \int (y \dot{B}_x' - E_z') dv, \dots \\ \int_{\infty} z (\vec{n} \times \vec{E}')_x d\sigma = - \int (z \dot{B}_x' + E_y') dv, \dots \end{cases}$$

$$(5, 22) \quad \int_{\infty} \vec{r} (\vec{n} \cdot \vec{B}') d\sigma = \int \vec{B}' dv.$$

Introducing this into (5, 15), (5, 16), (5, 17), and integrating we get

$$(5, 23) \quad \int_{\infty} (\vec{X} \cdot \vec{n}) d\sigma = - e \vec{E}_x' - \left[\vec{B}' \times \int \dot{\vec{D}}' dv \right]_x + \left[\vec{D}' \times \int \dot{\vec{B}}' dv \right]_x,$$

$$(5, 24) \quad \int_{\infty} (\vec{S} \cdot \vec{n}) d\sigma = - \vec{H}' \cdot \int \dot{\vec{D}}' dv - \vec{H}' \cdot \int \dot{\vec{B}}' dv,$$

$$(5, 25) \quad \begin{aligned} \int_{\infty} (\vec{N}_x \cdot \vec{n}) d\sigma &= \vec{B}' \cdot \int \vec{r} \dot{\vec{D}}_x' dv - B_x' \int (\vec{r} \cdot \dot{\vec{D}}') dv \\ &\quad - \vec{D}' \cdot \int \vec{r} \dot{B}_x' dv + D_x' \int (\vec{r} \cdot \dot{\vec{B}}') dv \\ &\quad + (\vec{B}' \times \int \dot{\vec{H}}' dv)_x - (\vec{H}' \times \int \dot{\vec{B}}' dv)_x \\ &\quad + (\vec{D}' \times \int \dot{\vec{E}}' dv)_x - (\vec{E}' \times \int \dot{\vec{D}}' dv)_x \\ &\quad + (\vec{m} \times \vec{B}')_x - e (\vec{r}_0 \times \vec{E}')_x \end{aligned}$$

Now from (1, 12) it follows that

$$(\vec{B}' \times \vec{H}') - (\vec{H}' \times \vec{B}') + (\vec{D}' \times \vec{E}') - (\vec{E}' \times \vec{D}') = 0;$$

hence (5, 25) reduces to

$$(5, 26) \quad \begin{aligned} \int_{\infty} (\vec{N}_x \cdot \vec{n}) d\sigma &= \vec{B}' \cdot \int \vec{r} \dot{\vec{D}}_x' dv - B_x' \int (\vec{r} \cdot \dot{\vec{D}}') dv \\ &\quad - \vec{D}' \cdot \int \vec{r} \dot{B}_x' dv + D_x' \int (\vec{r} \cdot \dot{\vec{B}}') dv \\ &\quad + (\vec{m} \times \vec{B}')_x - e (\vec{r}_0 \times \vec{E}')_x. \end{aligned}$$

If we substitute (5, 11), (5, 12) and (5, 23), (5, 24), (5, 26) into (5, 4) and (5, 5) we see that all terms containing volume integrals cancel one another,

and we get :

$$(5, 27) \quad \frac{d\vec{G}'}{dt} = e \vec{E}',$$

$$(5, 28) \quad \frac{d\vec{M}'}{dt} = (\vec{B}' \times \vec{m}) - (e\vec{r}_0 \times \vec{E}').$$

If \vec{M}' is referred to the singularity as origin, then $\vec{r}_0 = 0$, and the second term in the right hand side vanishes.

The energy has to be treated a little differently. We have

$$\begin{aligned} \frac{dE}{dt} &= \frac{d}{dt} \int U dv = \int \left(\frac{\partial U}{\partial \vec{B}} \cdot \dot{\vec{B}} + \frac{\partial U}{\partial \vec{D}} \cdot \dot{\vec{D}} \right) dv \\ &= \int (\vec{H} \cdot \dot{\vec{B}} + \vec{E} \cdot \dot{\vec{D}}) dv. \end{aligned}$$

Introducing here (5, 6) and (5, 9), we get

$$(5, 29) \quad \frac{dE}{dt} = \int (\vec{H} \cdot \dot{\vec{B}} + \vec{E} \cdot \dot{\vec{D}} + \vec{H}' \cdot \dot{\vec{B}}' + \vec{E}' \cdot \dot{\vec{D}}') dv.$$

If we now define the internal energy density as the value of the function $U(\vec{B}, \vec{D})$, for the arguments \vec{B}', \vec{D}' ;

$$(5, 30) \quad U' = U(\vec{B}', \vec{D}'),$$

and the total internal energy as

$$(5, 31) \quad E' = \int U' dv,$$

then

$$(5, 32) \quad \frac{dE'}{dt} = \int (\vec{H}' \cdot \dot{\vec{B}}' + \vec{E}' \cdot \dot{\vec{D}}') dv,$$

and (5, 29) becomes

$$(5, 33) \quad \frac{dE}{dt} = \frac{dE'}{dt} + \vec{H} \cdot \int \dot{\vec{B}}' dv + \vec{E} \cdot \int \dot{\vec{D}}' dv.$$

Substituting this and (5, 24) into (5, 4), we get

$$(5, 34) \quad \frac{dE}{dt} = 0$$

For the quasi-stationary case we have $\vec{G}' = E' \vec{v}$; therefore in the rest-system

$$(5, 34a) \quad E'_0 = \text{const.}, \quad \vec{G}'_0 = 0, \quad \text{for } \vec{v} = 0.$$

In the same way we treat the last equation (5, 5). We find

$$\begin{aligned} \frac{d}{dt} (\vec{E} \cdot \vec{q}_x) &= \frac{d}{dt} (\vec{E}^i \cdot \vec{q}_{x^i}) + \vec{H}^e \cdot \int x \vec{B}^i dv + \vec{E}^e \cdot \int x \vec{D}^i dv, \\ \vec{G} &= \vec{G}^i + (\vec{E}^e \times \int \vec{H}^i dv) - (\vec{H}^e \times \int \vec{E}^i dv), \\ \int_{\infty} x (\vec{S} \cdot \vec{n}) d\sigma &= - \vec{E}^e \cdot \int x \vec{D}^i dv + [\vec{E}^e \times \int \vec{H}^i dv]_x \\ &= - \vec{H}^e \cdot \int x \vec{B}^i dv - [\vec{H}^e \times \int \vec{E}^i dv]_x \\ &= - (\vec{E}^e \times \vec{m})_x. \end{aligned}$$

Substituting this into the equation mentioned, we get with regard to (5, 34a)

$$(5, 35) \quad \vec{E} \cdot \vec{q}^i = \vec{E}^e \times \vec{m}$$

(5, 27), (5, 28), (5, 34) and (5, 35) are the equations of motion in the rest-system of the singularity

To write them in a general coordinate system with velocity \vec{v} , we refer the angular momentum \vec{M}^i and the centre \vec{q}^i to the singularity \vec{r}_0 as origin (i.e., we take $\vec{r}_0 = 0$), then we introduce the space-time 4-vector

$$(5, 36) \quad (\vec{G}^i, \vec{E}^i) = (g_1, g_2, g_3, g_4),$$

and the space-time 6-vectors

$$(5, 37) \quad \begin{cases} (\vec{B}^e, \vec{E}^e) = (F_{23}, F_{31}, F_{12}; F_{14}, F_{24}, F_{34}), \\ (\vec{m}, \vec{p}) = (m_{23}, m_{31}, m_{12}, m_{14}, m_{24}, m_{34}), \\ (\vec{M}^i, \vec{P}^i) = (M_{23}, M_{31}, M_{12}; M_{14}, M_{24}, M_{34}); \end{cases}$$

\vec{p} and \vec{P}^i are defined by

$$(5, 38) \quad \begin{cases} \vec{p} = \vec{m} \times \vec{v}, \\ \vec{P}^i = \vec{E}^i \cdot \vec{q}^i. \end{cases}$$

Further we observe, that

$$(5, 39) \quad Q_k^l = f^{ln} m_{nk} - f^{kn} m_{nl}$$

is an antisymmetric tensor.

The covariant components Q_{kl} are

$$(5, 40) \quad (Q_{23}, Q_{31}, Q_{12}) = (\vec{B} \times \vec{m}) - (\vec{E} \times \vec{p}),$$

$$(5, 41) \quad (Q_{14}, Q_{24}, Q_{34}) = (\vec{E} \times \vec{m}) + (\vec{B} \times \vec{p}).$$

Now the equations of motion can be written

$$(5, 42) \quad \begin{cases} \dot{g}_k = e F_{kl} \dot{q}^l, \\ \dot{M}_{kl} = Q_{kl}, \end{cases}$$

where the dot means differentiation with respect to proper time; or in space-vector notation [omitting the indices (e) and (i)],

$$(5, 43) \quad \begin{cases} \frac{d\vec{G}}{dt} = e \left(\vec{E} + (\vec{v} \times \vec{B}) \right), \\ \frac{d\vec{E}}{dt} = e \vec{v} \cdot \vec{E}, \end{cases}$$

$$(5, 44) \quad \begin{cases} \frac{d\vec{M}}{dt} = (\vec{B} \times \vec{m}) - (\vec{E} \times \vec{p}), \\ \frac{d\vec{P}}{dt} = (\vec{E} \times \vec{m}) + (\vec{B} \times \vec{p}), \end{cases}$$

$$(5, 45) \quad \begin{cases} \vec{p} = \vec{m} \times \vec{v}, \\ \vec{P} = E\vec{q}. \end{cases}$$

6. Conclusion.

The equations (5, 44) and the first of (5, 45) are those given by Kramers;⁶ the second equation (5, 45) gives the physical interpretation of the quantity \vec{P} , introduced by Kramers quite formally, as the product of energy and the distance of the centre of energy from the singularity. The results of Kramers' paper hold also in our theory. quantisation of the angular momentum leads to Dirac's wave-equation for the electron, and the ratio of magnetic moment to angular momentum is e/μ , where μ is the rest-energy. But one meets deep difficulties in trying to interpret these results on the basis of the unitary field theory. It seems very probable and can be confirmed by strong arguments, that the high rest-energy of the heavy elementary particles, neutron and proton, is of magnetic origin.⁷ But there seems to be no solution of the field equations corresponding to a pure magnetic dipole. These questions will be discussed later.

⁶ H. A. Kramers, *loc. cit.*

⁷ M. Born, *Nature*, 1935, **136**, 952; *Proc. Ind. Acad. Sci., A*, 1935, **2**, 533.

THE RAMAN SPECTRA OF ORTHO-PHOSPHORIC ACID AND SOME PHOSPHATES.

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1 Introduction

IN a recent communication to these *Proceedings*,¹ the author studied the progress of electrolytic dissociation and the effect of polymerisation on the Raman spectrum of iodic acid. This investigation has been extended to other inorganic acids and the present paper deals with the results obtained with ortho-phosphoric acid (H_3PO_4). The Raman spectrum of this acid has been investigated by Nisi² who obtained frequency differences* of 356, 498 and 911 for 84%, 512 and 906 for 50% and 505 and 895 for 25% solutions. These results have been confirmed quite recently by Jeppesen and Bell³. But in spite of the attempts of several workers to obtain the Raman spectra of the three series of salts of this acid corresponding to the stepwise substitution of the three hydroxyl hydrogen ions, it is surprising that only two of them have so far yielded positive results. Nisi obtained four lines at 358, 518, 889 and 1061 for a 38% solution of dihydrogen-sodium phosphate and Schæfer and his co-workers⁴ observed one line at 924 for the crystals of the tertiary phosphate of ammonium. Thus the Raman spectra studies of this acid and its salts are obviously incomplete.

2 Experimental Arrangements

One of the chief difficulties experienced by the earlier investigators in obtaining the Raman spectra of phosphoric acid⁵ and the phosphates is the strong continuous spectrum which appears on every plate and masks all faint lines. As mentioned in the previous communications, the pyrex mercury arc designed and used by the author gives much less background than the quartz burners usually employed and have been helpful for giving

¹ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1935, 2, 119

² Nisi, H., *Jap. Jour. Phys.*, 1929, 5, 119

* The numbers in this and the following pages denote frequency shifts in cm^{-1}

³ Jeppesen, M. A., and Bell, R. M., *Jour. Chem. Phys.*, 1935, 3, 363.

⁴ Schæfer, Matossi and Aderhold, *Zeit. f. Phys.*, 1930, 65, 289

⁵ Hibben, J. H., *Jour. Amer. Chem. Soc.*, 1931, 53, 2418.

the very long exposures that are necessary in the present work. The constructional details of the arc are given in Fig 1. Three electrodes A, B and C

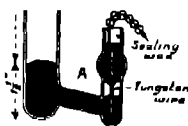
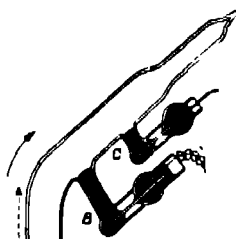


FIG 1.

are joined to a thick walled pyrex tube of $\frac{3}{4}$ " diameter and 12" long which is bent to the form illustrated. After the introduction of freshly distilled mercury, the tube is evacuated thoroughly for about six hours while the arc is kept running hot and finally sealed off at a vacuum higher than 10^{-5} mm. The electrodes A and C are connected to an induction coil for starting the arc and A and B are connected to 220 volt mains through a rheostat in the usual manner. The arc is run in the vertical position and the mercury distilling from it fills the cathode at the top and overflows, thus keeping a constant level for the cathode. The electrode C may also be dispensed with and the arc started by tilting it in the direction of the arrow. These lamps are found to be very efficient for recording faint lines in crystals and solutions, where the intensity of the unmodified light is enormously great and are quite reliable for continuous use. A slow stream of air directed to the top alone helps to diminish the continuous spectrum further. The general experimental method is the same as for the previous investigations of the author.

3 Results

The purest sample of ortho-phosphoric acid supplied by E. de Hæn was used as such and its Raman spectrum was obtained for a wide range of concentrations varying from 85% (by weight) to 3%. The product of the time of exposure and the concentration was kept constant throughout. The results are given in Table I. The intense line which appears at all concentrations gradually shifts from 914 to 876 in passing from 85% to 3% solution.

TABLE I.
Ortho-phosphoric Acid H_3PO_4

Concentration (% by weight)	Raman lines in cm^{-1}							Remarks
85%					914 st	495 v w,d	361 v w,d	Strong continuous spectrum
60%					903 st	495 w,d	361 v w,d	"
30%	..	1200	— (band)	950	890 v, st	495 m,d	361 w,d	Water bands appear
15%	1427 v w	1194 w,d	1082 w	959 w	886 v st	495 w,d	361 w,d	Water bands strong
7.5%	1427 v w	1194 w,d	1082 w	959 w	886 st	495 w,d	361 v w,d	
3%	1082 v,w	959 v w	880 st	"

st=strong, *v st*=very strong; *m*=medium, *w*=weak, *v w*=very weak, *d*=diffuse.

It is also qualitatively observed that the intensity of this line increases as the concentration falls off to about 10%. Two other weak and diffuse lines at 495 and 361 appear unshifted at all concentrations. A broad but weak band with a frequency shift of about 950–1200 makes its appearance at about 30% and breaks up into three weak and diffuse lines of frequency differences of 1194, 1082 and 959. Due to the extreme feebleness of these lines their intensity variations on dilution could not be determined. A spectrum of the acid taken with *p*-nitro-toluene as filter to cut off the 4047 radiations, shows a faint line at 1427. The water bands at 3220, 3435 and 3596 brighten up as the dilution increases and the intensities of the bands at 3220 and 3435 are also greater than for the pure water. The increase in the intensity of 3220 is evidently due to the superposition of the weak line at 1427 on this band and the intensity of 3435 is probably enhanced by the vibrations of the OH groups in the acid itself.

Phosphates —The crystals of the secondary and tertiary phosphates of sodium, potassium and ammonium were prepared from the corresponding primary salts by the addition of the calculated amount of alkali and purified by repeated crystallisations. The results are given in Table II. The crystals yielded only very weak lines even on prolonged exposure and except in the case of tertiary phosphates, their Raman lines are not included in the Table. The exposure time for the aqueous solutions varied from 24 hours to 48 hours.

TABLE II.
Phosphates.

Substance	Raman lines in cm^{-1}					Crystal
Na_3PO_4 17%	1085 v w	971 m	..			956 w
K_3PO_4 20%	.	984 m	944 m,d			968 w 944 w
$(\text{NH}_4)_3\text{PO}_4$ 31%	1080 v w	985 m		515 v w	363 v w	951 w
Na_2HPO_4 17%	1085 w	971 m	886 v w	
K_2HPO_4 17%	1070 w	965 st	889 w	
$(\text{NH}_4)_2\text{HPO}_4$ 30%	1070 w	975 st	889 w	515 v w	363 v w	
$\text{NaNH}_4\text{HPO}_4$ 20%	1085 w	975 m	889 v w	515 v w	..	
NaH_2PO_4 27%	1085 m	..	886 st	495 w	356 w	
KH_2PO_4 20%	1080 m		869 st	510 w	360 w	
$\text{NH}_4\text{H}_2\text{PO}_4$ 30%	1090 m	..	885 st	515 w	360 w	

4 Discussion of Results.

From the results obtained for the three series of salts of phosphoric acid it is to be inferred that while the three lines at 1085, 495 and 356 appear more or less in the same position in all cases, the intense line shifts from about 885 in the primary salt to about 985 in the secondary and tertiary salts. In the secondary salts the line at 886 is also feebly present. The intensity of the line at 1085 varies from a medium strength in the dihydrogen phosphates to weak in the secondary salts and is very weak in the tertiary salts. These results show that 1085, 980 (*st*), 515 and 363 are the characteristic frequencies of the PO_4 radical 1080, 975(*st*), 889 (*w*), 515 and 363 of the HPO_4 ion and 1085, 885 (*st*), 515 and 360 of the H_2PO_4 ion. In the Raman spectrum of the acid, the strongest line which is present even in the lowest concentration, namely 3%, is the one at about 889, which indicates, as shown by Nisi,^a that H_2PO_4 ions predominate at all dilutions. This line is, however, strongly influenced by the concentration of the acid as is shown by a shift of about 34 wave-numbers while passing from 85% to 3%. The appearance of the band between 950–1200 at a concentration of 30% and its further splitting up into three lines in lower concentrations, two of which, namely, 959 and 1082, correspond to those of HPO_4 ion, suggests that the further ionisation

^a Nisi, H, *loc. cit.*

of $\text{H}_2\text{PO}_4' \rightarrow \text{H}' + \text{HPO}_4''$ begins at this stage. This band may be present also at higher concentrations and is probably masked by the continuous spectrum. The percentage of ionisation from $\text{H}_2\text{PO}_4' \rightarrow \text{HPO}_4''$ remains, however, low even in very dilute solutions as is shown by the weakness of the line at 975. These facts are also in agreement with other physico-chemical measurements.⁷ The weak line at 1427 and the increased intensity of the water band at 3435 are, as indicated earlier, due to the OH in the structure of the incompletely ionised acid.

5. The Structure of Phosphates

In Table III, the Raman frequencies ascribed to the PO_4 radical are compared with those of sulphates and selenates.⁸ The force constants calculated on the basis of Dennison's dynamical theory are also given. It can be seen from these results, that a close correspondence exists between the frequencies and the force constants of these three radicals indicative of a

TABLE III.

Ion	Raman lines in cm^{-1}				$f \times 10^{-5}$	$f' \times 10^{-5}$	$P \times 10^{-5}$
	ν_1	ν_2	ν_3	ν_4			
PO_4'''	985	361	1085	515	5.23	0.967	0.185
SO_4''	983	342	1115	623	4.57	1.14	0.74
SeO_4''	835	447	875	415	4.22	0.59	0.51

tetrahedral structure for the PO_4''' ion as in the case for the SO_4'' . The infra-red measurements⁹ of lithium phosphate give reflection maxima at about 9.25μ and $16\mu - 19.1\mu$ which correspond fairly closely to the active frequencies 1085 and 515 in the Raman effect. But the slight variations in the frequency shift, 980, of the symmetrical oscillation in the presence of different cations, namely, potassium, sodium and ammonium, are probably due to a small deviation from the tetrahedral symmetry.

In conclusion, the author wishes to thank Prof. Sir C. V. Raman for his interest in the work.

⁷ Mellor, *Treatise of Inorganic Chemistry*, Vol. VIII.

⁸ Ganesan, A. S., *Proc. Ind. Acad. Sci. A*, 1934, 1, 156.

⁹ Langford, G., *Phys. Rev.*, 1911, 33, 137.

Summary.

The Raman spectra of ortho-phosphoric acid for a wide range of concentrations and of the primary, secondary and tertiary phosphates of potassium and ammonium have been obtained. The acid lines which indicate the ionisation of $\text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$ and the ionisation of $\text{H}_2\text{PO}_4^- \rightarrow \text{H}^+ + \text{HPO}_4^{2-}$ are observed. Weak lines characteristic of the acid have also been observed. The phosphates give characteristic spectra which are identified as due to PO_4^{3-} ions. The frequency shifts of the PO_4 radical are compared with those of SO_4 and SeO_4 and the force constants are evaluated.

THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS—III.

β -Clausenan and γ -Clausenan.

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AND

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THE volatile oil from the leaves of *Clausena Willdenowii*, W. and A. collected in winter has been shown to consist of three new compounds, α -, β - and di- α -clausenans belonging to the furan group¹. The leaves of the same plant grown in a different locality and collected at the same time of the year, however, yielded a similar product but without any appreciable quantities of α -clausenan. The analytical constants of the three new oils (III, IV and V) and of the two previous samples (I and II) have been given in Table I and indicate apparent identity between them. The constants for the product obtained by extraction of the distillation water which dissolves out mainly the pleasant smelling esters have also been given. The new samples on fractionation behave like the previous specimens, as shown in Table II, three groups of products being obtained 104°/50 mm., 80–125°/10 mm., 190°/10 mm. The first fraction was found to be a mixture of β -clausenan and a new body hereafter called γ -clausenan which is the main constituent and is a clear colourless liquid having an odour of unripe mangoes. The next fraction consisted mainly of esters and ketones and the last of di- α -clausenan.

According to Wienhaus² the atomic refraction constant for furan oxygen is 1.2, being lower than for ethereal oxygen (1.642) in most other compounds. The molecular refractions of the clausenans taking the usual value and Wienhaus's constant are as follows:

¹ *Proc. Ind. Acad. Sci.*, 1934, 1, 186.

² *Ber.*, 1920, 53, 1660.

	d_4^{20}	n_D^{20}	$(R_L)_D$ Found	$(R_L)_D$ Calculated	
				0=1.643	0=1.2
α -Clausenan	0.9026	1.4722	45.96	45.96	45.51
γ -Clausenan	0.9050	1.4739	45.98	45.96	45.51
Di- α -Clausenan	1.0196	1.5468	89.95	90.18	89.29

It is found that the values are in good agreement with the usual value for ethereal oxygen. It has also been observed by Eisenlohr that the depression of molecular refraction observed in furan and pyrone decreases in their dimethyl derivatives and it is possible that in the higher homologues, this depression vanishes and the usual value for ethereal oxygen becomes valid.

The parachor was found to be 382.8 at 30° and 387.8 at 50° the calculated value being 386.8, the higher value at 50° indicating that γ -clausenan is an associated liquid. It has nearly the same viscosity as α -clausenan. The vapour pressures between 80-180°, Ramsay and Shield's constant and other properties have been determined and will be found in the experimental part. Dioxan was found to be unsuitable as a solvent for molecular weight determination of these compounds.

Pure γ -clausenan keeps well in the absence of oxygen and is miscible with most organic solvents. It has somewhat higher physical properties and differs from α - and β -clausenans in not forming an addition compound with either ferrocyanic or ferricyanic acids. It could be easily separated and purified by this process from β -clausenan with which it is mixed up. While α -clausenan was unaffected by sodium and alcohol, the γ -isomer was reduced to a tetrahydro-derivative. The reduction product gave the Liebermann colouration and with bromine in chloroform solution, the same colour changes as those observed with α -clausenan, showing the presence of the furan nucleus. No ketone was obtained by oxidation with potassium permanganate, as in the case of α -clausenan. Like most furan compounds γ -clausenan is also gradually resinified in the presence of acids and is unaffected by boiling acetic anhydride, alkalis and water. As γ -clausenan does not react with ferrocyanic acid, it was possible to obtain β -clausenan pure. Its properties along with those of its acetyl derivative have been described.

Experimental

The analysis of oils obtained from three lots of leaves collected in winter from a different locality and immediately distilled have been given in Table I (III, IV and V), along with constants, for the samples previously examined, which show that they are similar

TABLE I

Sample No.	III	IV	V	I	II
d_{30}^{30}	0.9349	0.9333	0.9340	0.9317	0.9341
n_D^{30}	1.5129	1.5111	1.5112	1.5114	1.5112
$[\alpha]_D^{30}$	-1.6°	-2.1	-1.9	-1.1	-0.2
Acid value	0.3	0.2	0.4	0.4	1.2
Ester value	9.5	9.1	9.1	9.2	13.4
Acetyl value	22.2	23.7	20.1	13.2	24.4

Appreciable quantities of the oil were dissolved in the distillation water. The oil (10 g) extracted from 8 litres of distillation water had the following properties d_{30}^{30} , 1.086, n_D^{30} , 1.5182, acid value, 7.9, ester value, 220.1. The esters appear to be particularly soluble in water

Distillation of the oil —The oil (sample III, 490 g) was fractionated three times with an eight pear Young's column at 50 mm in the first stage, and at 10 mm. later from a Claisen flask, the following fractions being obtained :

TABLE II.

Fraction	B.P	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	Yield per cent on original oil
1	101—103°/50 mm.	0.8984	1.4832	+ 0.0°	50	10.2
2	103—104	0.9107	1.4840	- 0.4	100	20.4
3	104—105	0.9152	1.4882	+ 0.4	170	34.7
4	84—87/10 mm.	0.9226	1.4914	+ 0	20	4.1
5	87—105	0.9304	1.5106	-- 8.6	10	2.0
6	105—185	0.9350	1.5140	--18.2	5	1.0
7	188—193	1.060	1.5406	--	130	26.5

TABLE III.

γ -Clausenan		β -Clausenan	
Temperature °C.	Vapour pressure mm	Temperature °C	Vapour pressure mm
82.0	27.0	70.0	19.5
95.0	41.0	85.0	38.0
102.0	52.5	97.0	65.5
112.0	74.0	99.0	72.0
119.5	106.5	101.0	82.0
125.5	127.0	125.0	172.0
129.0	145.0	131.0	207.5
135.0	180.0	138.0	258.0
139.0	210.0	148.0	318.0
143.0	235.0	151.0	412.5
144.5	265.0	158.0	458.0
151.0	314.0	161.0	496.0
156.0	360.0	168.0	597.0
159.0	394.0	171.0	644.0
163.5	449.0	174.0	696.0
165.5	474.5	176.0	734.5
171.0	548.0		
173.0	585.0		
175.0	607.5		
177.5	647.0		
180.0	684.0		

β -Clausenan—Since the new samples were free from α -clausenan, it seemed possible that β -clausenan will be more easily obtained pure as the other compounds accompanying it do not react with ferrocyanic acid. Fraction I was treated with pure ferrocyanic acid and the addition compound decomposed with sodium carbonate and the liberated product was fractionated over sodium when β -clausenan having the following properties was obtained. b p 96–97/50 mm, d_{40}^{30} , 0.8805, d_4^{30} , 0.8768, d_{50}^{30} , 0.8701, d_4^{50} , 0.8589, $[\alpha]_D^{30}$, +3.0, n_D^{30} , 1.4681, γ_{30} , 27.4, γ_{50} , 27.2; η_{30} , 0.090. Analysis: C, 79.46, H, 9.9; $C_{10}H_{14}O$ requires C, 80.0, H, 9.33. The vapour pressures have been given in Table III.

The parachor was 396.8 at 30° and 403.9 at 50° in fair agreement with the calculated value 397.4 according to Mumford and Philips and 406.4 according to Vogel.

Acetylation of β -clausenan— β -Clausenan (5 g) was boiled for an hour with acetic anhydride (10 c.c.) and sodium acetate (1.0 g). The acetylated product distilled at 105°/32 mm., d_{30}^{30} , 0.9481, n_D^{30} , 1.4672, acetyl value 265, showing that the sample is quantitatively acetylated. Though β -clausenan is not as unsaturated as α -clausenan, it is more amenable to resinification and oxidation.

γ -Clausenan—The major portion of the fractions failed to react with freshly prepared ferrocyanic acid. The unreacted portion (270 g) on fractionation over sodium was found to be homogeneous and had the following properties given in (a), and (b) gives the properties of α -clausenan for comparison:

	B P at 50 mm	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	$(R_L)_D$
(a)	103–104°	0.9089	1.4739	nil	45.98
(b)	102	0.9065	1.4722	,,	45.96

Analysis of (a) C, 81.70, H, 8.40, $C_{10}H_{12}O$ requires C, 81.81; H, 8.18. It is not identical with α -clausenan having somewhat higher physical properties and is hereafter called γ -clausenan. It is unaffected by boiling with acetic anhydride, alkalis or water in a sealed tube. It gives the Liebermann test and with an acetic acid or chloroform solution of bromine, gives a purple colouration changing to blue and finally green, being similar in these respects to α -clausenan. Unlike the latter, however, γ -clausenan does not combine with ferrocyanic or ferricyanic acids.

Viscosity and surface tension of γ -clausenan—They were measured by means of an Ostwald viscometer calibrated with benzene at 30° as in the case of α -clausenan. The time of flow for γ -clausenan was 105 seconds, being an average of four readings. The viscosity was found to be 0.0085 c g s.

The difference in the equilibrium levels in the capillary limb and the lower viscometer bulb was 29.6, 28.8 and 64.2 and 61 mm for γ -clausenan and water respectively giving a surface tension of 29.92 at 30° and 29.10 at 50° .

The parachor was found to be 382.8 at 30° and 388.0 at 50° , the calculated values being 386.8 from Mumford and Philips and Vogel's data.³

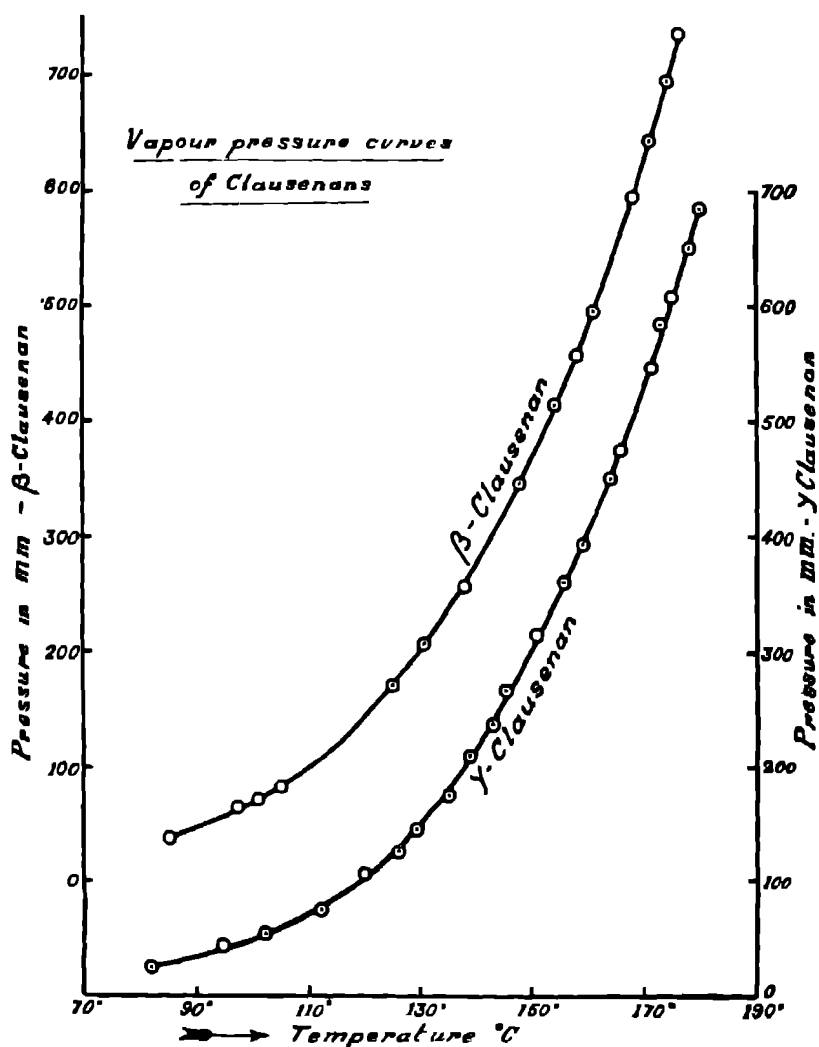


FIG. 1.

The molecular refraction was found to be 45.98, identical with the calculated value 45.96, taking for the furan oxygen Eisenlohr's value 1.643

³ J. C. S., 1929, 130, 2112; 1934, 135, 334.

for ethereal oxygen. If Wienhaus's value 1.2 is taken for the furan oxygen, the value for molecular refraction is depressed by 0.44

The Ramsay and Shield's constant was found to be somewhat high being (a) 2.43 by application of Ramsay and Shield's equation, (b) 2.46 by Walden and Swinne's method⁴. The critical temperature by Guldberg rule is 412°. The molecular latent heat of vapourisation from Trouton's rule modified by Wartenburg⁵ ($L = 7.4T \times \log T$) was found to be 10,650 calories at 30°. The value from the formula

$$L = \frac{1.985T_1T_2}{T_2 - T_1} l'' \frac{p_2}{p_1}$$

based on Clausius-Clapeyron equation was 10,730 calories at 98°C. The molecular volume, using Kopp's constants was 183.8, the experimental value being 148/0.7884 or 186.3

The vapour pressures of γ -clausenan between 80-180° have been measured by the submerged bulb method of Smith and Menzies⁶ and the values recorded in Table III. Fig 1 shows the vapour pressure curves of the clausenans

Reduction of γ -Clausenan—On reduction with sodium and alcohol tetrahydro- γ -clausenan having the following properties was obtained: b.p. 105/100 mm, d_{20}^{20} , 0.8957, n_D^{20} , 1.4698; C, 78.72; H, 10.22, $C_{10}H_{16}O$ requires C, 78.95, H, 10.52. α -Clausenan was not reduced by this process.

Oxidation with potassium permanganate—No trace of the ketone $C_9H_{10}O$ obtained from α -clausenan was formed. The products were exclusively acidic and resinous and were not further examined

Summary

The analyses of three samples of the volatile oil from *Clausena Willdenowii*, W & A have been given. A component $C_{10}H_{12}O$, called γ -clausenan, isomeric with α -clausenan and belonging to the furan group has been isolated from the oil. Its physical properties as well as methods for separating it from α - and β -clausenans have been described. β -clausenan has been obtained pure and its properties determined.

⁴ Z. Physik Chem., 1913, 82, 290.

⁵ Z. Electrochem., 1914, 20, 444.

⁶ J. Am. Chem. Soc., 1910, 32, 1448.

BRUCINE SULPHATE AS AN INTERNAL INDICATOR IN TITRATIONS WITH STANDARD DICHROMATE SOLUTION.*

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THE elegant method of determining iron volumetrically with permanganate cannot be employed in the presence of hydrochloric acid except after the addition of manganous sulphate and phosphoric acid. This procedure, however, has not found general favour and in spite of the disadvantage in the use of an external indicator, dichromate method has more or less been universally adopted. The discovery of diphenylamine as an internal indicator in such titrations (Knop, 1924) was therefore a great advance in this field. This substance gives an intense blue colour when treated with a drop of 0.1 normal solution of potassium dichromate in hydrochloric acid or sulphuric acid containing trivalent iron. The addition of excess of ferrous salt decolourises the indicator so that back titration is possible. Recently Phenanthroline has been studied in detail as an indicator in oxidimetry (Walden and Edmonds, 1935) and has been found to be very satisfactory. But the difficulty with which it is synthesised is for the present against its widespread use.

Though with a strict adherence to the optimum conditions (Sarver, 1927) one may obtain satisfactory results with diphenylamine, there are certain drawbacks in its use. In the presence of the green colour of the chromic salt and the yellow of the ferric salts the end point frequently ceases to be sharp and considerable difficulty is experienced in judging it even after the addition of phosphoric acid. An indicator giving a more easily detectable colour, which is not masked by the chromic or ferric salts, should be more valuable and one such has been found in Brucine. 1 c.c. of a 1 per cent.

* After our work described in this paper had been completed, it was realised that the use of Brucine as an internal indicator had been indicated by Seikichi Miyagi (*J. Soc. Chem. Ind. Japan* 36, suppl. binding 1933, 146-47). Since, however, the Japanese author had not examined the scope of the method in detail, we thought it would be useful to publish our results.
—T. R. S.

solution of brucine in 100 c.c. of water containing sulphuric acid is coloured a distinct red with one drop of N/100 dichromate solution. This red colour is quite easily visible in the presence of chromic and ferric salts and there is no need to add phosphoric acid as in the case of diphenylamine indicator in order to improve the sharpness of the end point.

The indicator solution is prepared by dissolving one gram of brucine in 100 c.c. of 3 N sulphuric acid and preserved in a stoppered amber coloured bottle. The colourless solution turns pale brown on standing without however losing its usefulness. It is not desirable, however, to prepare more than 100 c.c. at a time. It is further noticed that the indicator functions best only after standing for a few hours after it has been made. Its use in the different methods employing dichromate titrations is illustrated below. 10 drops of the brucine solution are used as indicator. When titrating ferrous salts against dichromate, near the end point—within 3 drops of it—the solution changes to a dirty green and with the first excess drop of dichromate the solution becomes red. The faintest trace of red is easily detected in the presence of the green chromic salt. It is necessary that the acid strength of the solutions is not allowed to fall below 2 normal, though above that it may be allowed to vary within wide limits. Back titration using this indicator is not quite sharp probably due to the oxidation product not undergoing reduction easily.

TABLE I

Wt. of Ferrous am. sulphate in grams	Vol. of 0.1015 N KMnO ₄ in c.c. (a)	Vol. of 0.1 N Dichromate in c.c. (b)	Fe calculated in grams	
			From (a)	From (b)
0.2025	5.05	5.15	0.0286	0.0288
0.4104	10.05	10.20	0.0570	0.0570
0.6060	15.15	15.35	0.0858	0.0857
0.9015	22.60	23.00	0.1280	0.1284
1.2500	31.25	31.70	0.1771	0.1770
1.8050	45.25	46.00	0.2564	0.2569

Table I compares the results obtained by titrating varying amounts of ferrous ammonium sulphate against standard permanganate on the one hand, and dichromate using brucine sulphate as internal indicator on the other.

The agreement between the two methods is quite close. The colour due to the ferric iron does not affect the sharpness of the end point and this

is further confirmed by adding known large quantities of ferric chloride to the ferrous salt solution that has to be titrated

TABLE II.

Concentration of dichromate solution 0.1 N

Concentration of ferric chloride 0.2 N.

Concentration of ferrous ammonium sulphate 0.1 N

Vol. of FeCl ₃ added in c.c.	Vol. of Ferrous am. sulphate in c.c.	Vol. of water in c.c.	Vol. of 0.1 N dichromate required in c.c.
10.0	25.0	70	25.00
20.0	25.0	60	25.05
40.0	25.0	40	25.05
80.0	25.0		25.05

The indicator is therefore useful in the estimation of chrome-iron alloys and ores in which the ferric iron is present in large quantities and has been utilised by us for the analysis of the ore

Mercuric chloride, mercurous chloride and stannic chloride do not affect the end point and this was settled by analysing a ferric chloride solution in two ways — (1) the iron was precipitated as ferric hydroxide, filtered, washed and dissolved in 1 : 1 sulphuric acid and after reduction with arsenic-free zinc titrated against standard permanganate, (2) the solution was reduced with stannous chloride, excess of the stannous salt oxidised with mercuric chloride and then titrated against potassium dichromate using brucine sulphate as indicator. The comparative results are given in Table III and they are very concordant

TABLE III.

Vol. of FeCl ₃ in c.c.	0.1015 N permanganate in c.c. (1)	0.1 N dichromate in c.c. (2)	Amount of iron present in grams	
			From (1)	From (2)
10.0	16.95	17.30	0.0961	0.0966
10.0	17.00	17.25	0.0963	0.0963
25.0	42.60	43.25	0.2415	0.2414
25.0	42.45	43.20	0.2410	0.2417

The above fact was further proved by analysis of samples of Kahlbaum's purest specimen of iron wire. The wire was converted into ferric chloride and the iron estimated as above using dichromate and brucine

TABLE IV.

Wt of iron wire in gms.	0.1113	0.1365	0.1893	0.2632
0.1 N $K_2Cr_2O_7$ in c.c. ..	20.50	24.40	33.90	47.10
Fe%	100.1	99.82	100.0	99.90

Titration of ferrous iron in the presence of hydrochloric acid with permanganate is possible when diphenylamine is used as indicator and brucine can be employed for the same purpose with equal advantage. Chlorine that may be liberated from hydrochloric acid affects the indicator just as any other oxidising agent and acts as so much permanganate. Table V records data obtained to illustrate this aspect of the use of brucine

TABLE V

Ferric chloride solution reduced with stannous chloride etc, and titrated against 0.1015N potassium permanganate.

Vol of Ferric chloride soln in c.c.	Vol. of Pot permanganate in c.c.	Amount of iron	
		Found in gm	Taken in gm
10.0	16.90	0.0958	0.0965
10.0	17.00	0.0963	0.0965
25.0	42.55	0.2412	0.2415
25.0	42.50	0.2409	0.2415

Application to soil analysis—As a rapid approximate method for the estimation of soil organic matter Schollenberger (1927) recommends the oxidation of the organic matter with excess of chromic acid and estimation of the excess of the oxidant by titration with ferrous ammonium sulphate using diphenylamine as indicator. It is now found that brucine can be used for the purpose with advantage. After the oxidation is over, the chromic acid solution is diluted, a known excess of ferrous ammonium sulphate solution is added and the excess of the ferrous salt titrated against standard dichromate. Direct titration of the chromic acid with ferrous sulphate is not possible with

brucine as indicator and is not very advisable even with diphenylamine since undesirable oxidation products are formed. Concordant results are obtained with brucine as shown below :—

TABLE VI.

	Wt. of soil sample	Per cent C-content	Deviation from the Mean
A. Low Grade	0.5005	2.50	-0.03
	0.3080	2.48	-0.05
	0.4254	2.60	0.07
	Mean	2.53	
B. High Grade	0.3112	5.06	0.05
	0.4215	5.02	-0.01
	0.3915	4.96	-0.05
	Mean	5.01	

Summary

Brucine sulphate has been shown to be a good internal indicator for titrations with dichromate and in certain respects superior to diphenylamine. The colour change from green to bright red at the end point is much more pronounced than the change from green to blue in the case of diphenylamine.

It has been shown that in titrations with potassium permanganate solutions, the disturbing effects due to the presence of hydrochloric acid may be obviated by using brucine as an internal indicator. The presence of ferric iron has not been found to interfere with the sharpness of the end point.

The use of this indicator in the analysis of chromium ores and in the estimation of organic matter in soils by the Schöllenberger method has been indicated.

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OPTIC MOMENTS OF ORGANIC MOLECULES IN RELATION TO CRYSTALLINE AND MAGNETIC BIREFRINGENCE.

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1 Introduction

IN a previous communication (Ramanadham, 1934), the author had shown how the principal refractive indices of a crystal could be correlated with the principal optic moments of the molecules constituting it and their orientation inside. As a particular case, the optic moments of the naphthalene molecule were deduced on the one hand from the known (1) refractive index, (2) the magnetic birefringence of the substance in the liquid state, and (3) the depolarisation of the light scattered by its vapour, and on the other hand from the observed principal refractive indices of the crystal together with the known orientations of the molecules. Agreement was found to be fair between the sets of optic moments deduced by these two entirely different methods.

It appears desirable to extend this treatment to a number of other organic crystals. As a preliminary to it, has been here undertaken the determination of the magnetic birefringence of organic solids in solution with carbon tetrachloride as the solvent. The choice of the solvent is based on the fact that carbon tetrachloride is known to exhibit no detectable magnetic double refraction. The substances are specially chosen from among those whose magneocrystalline behaviour has been studied by Krishnan.

2 Experimental

The experimental arrangement is the same as that adopted in the author's previous investigations (Ramanadham, 1929). The method of estimation of the positive double refraction exhibited by the aromatic compounds is, however, slightly different in the present arrangement. Instead of compensating the double refraction by compressing a plate horizontally, the compensation is now made more conveniently by elongating a glass plate vertically by weights hung from it. All the measurements are made with respect to benzene and the absolute values calculated by assuming the value of C_M for benzene as 5×10^{-13} at 30°C .

To prepare solutions of definite concentration, a measuring flask of 25 c.c. capacity, provided with a ground-glass stopper, is taken and into it is put a weighed quantity of the substance under investigation. Then carbon tetrachloride liquid is run down from a burette into the flask and after dissolving the substance, the volume of the solution is made up to 25 c.c. by further running down the required amount of CCl_4 . At the same time, the total volume of CCl_4 run down is noted.

As the refractive indices of the solutions are required in the calculations, they have been determined with an Abbe refractometer.

3 Results

The results are exhibited in the following table —

Substance	Temperature	Weight of the substance in 25 c.c. of the solution	Volume of CCl_4 in 25 c.c. of the solution	Refractive index of the solution for the D line	$C_M \times 10^{11}$
Naphthalene	27°·5 C	2·5 g	22·5 c.c.	1·4729	3·1
"	27°·5 C	4·0 "	20·8 "	1·4834	4·6
Diphenyl	30° C	8·0 "	17·5 "	1·5084	4·0
Acenaphthene	30° C	3·0 "	22·2 "	1·4770	1·0
Benzil	32° C	2·9 "	22·5 "	1·4728	1·5
Salol	32° C	7·0 "	19·4 "	1·4910	2·1
Benzophenone	29° C	7·0 "	19·1 "	1·4990	2·1
Phenanthrene	31° C	2·5 "	22·9 "	1·4822	3·1

4 Discussion

(a) *Naphthalene* — It is desired to see how far the observed values of C_M in the case of naphthalene solutions agree with those obtained by Salceanu (1932) in molten naphthalene. In calculating the magnetic birefringence to be expected for naphthalene solutions, we will accordingly make use of the optic moments $b_1 = 25·85 \times 10^{-24}$, $b_2 = 22·25 \times 10^{-24}$ and $b_3 = 9 \times 10^{-24}$ derived by the author in an earlier paper (*loc cit*) on the basis of Salceanu's value of C_M for molten naphthalene.

Applying the formula*

$$C_M = \frac{1}{20} \cdot \frac{n^2 - 1}{n\lambda kT} \cdot \frac{\nu_1[(a_1 - a_2)(B_1 - B_2) + \dots] + \nu_2[(a_1' - a_3')(B_1' - B_2') + \dots]}{\nu_1(b_1 + b_2 + b_3) + \nu_2(b_1' + b_2' + b_3')}$$

* This formula for the magnetic birefringence of solutions is taken from M. Ramanadham, *Ind. Jour. Phys.*, 1929, 4, 109.

the values of C_M for naphthalene solutions at the two concentrations for which observations have been made are calculated and shown below .—

Wt. of the naphthalene in 25 c.c. of the solution	Observed $C_M \times 10^{11}$	Calculated $C_M \times 10^{11}$
2.5 g.	3.1	2.5
4.0 „	4.6	3.9

The agreement between the observed and calculated values is fair within the degree of experimental error. In making the calculation, it is assumed that the carbon tetrachloride molecule is optically and magnetically isotropic, that the second term in the numerator vanishes, and that the second term in the denominator becomes $\nu_2 \cdot 3b'$ where b' is the optic moment of the carbon tetrachloride molecule in the gaseous condition, this can be deduced from the known refractive index of the liquid at the known density by applying Lorentz's equation

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{3}{4\pi\nu} = b'$$

The values of B_1 , B_2 , B_3 are obtained from equations of the form $B_1 = b_1(1 + p_1 x)$, where x is the optical susceptibility of the solution. The values of p_1 , p_2 and p_3 are the same as those used previously, namely, 1.8, 2.8 and 8.0

(b) *Diphenyl*.—From a study of the magnetic anisotropy of the crystal, Krishnan (1933) has been led to place the length of the molecule at an angle $20^\circ.1$ from the C axis and the breadth in the plane of the molecule at 31° to the b axis. This orientation has been confirmed by Dhar (1932) by X-ray analysis.

The refractive indices of the crystal are given by Narasimham (1931) as 1.554, 1.586 and 1.647. He has also given certain data regarding the disposition of the principal axes of the optical ellipsoid and the optic axes but these are not consistent amongst themselves. Hendricks and Jefferson (1933) who subsequently repeated the measurements on the crystal found the refractive indices to be 1.5598, 1.6542 and > 1.90 . These authors do not, however, give any information regarding the disposition of the principal optic axes with reference to the crystallographic axes. Groth has recorded that the optic axes make $20^\circ.75$ and $57^\circ.75$ respectively with the normal to the 001

face where the interference figure is viewed through cedar oil (Refractive index 1.515)

An attempt is made in the present investigation to decide between the conflicting results regarding the refractive indices and to fix the directions of the principal axes of the optical ellipsoid by making the following observations

The apparent angle made by one of the optic axes with the normal to the plate is measured as $31^{\circ} \cdot 8$ by mounting the crystal on a Fedorov stage under the microscope and tilting it until the corresponding melatope coincides with the intersection of the crosswires. This reading is in agreement with the angle $20^{\circ} \cdot 75$ given by Groth if we take into account the fact that the latter has been measured under cedar oil of refractive index 1.515

It is further noticed that the interference figure shown by a diphenyl crystal of thickness 0.109 mm between crossed nicols exhibits 13 complete rings. The double-refraction in the plate, *i.e.*, in 001 plane becomes then .0701.

To see which set of refractive indices gives this observed double refraction .0701 in the (001) plane, the true angles made by the optic axes with the normal are calculated with the aid of each one of the alternative values available for the intermediate refractive index, assuming the apparent angles given by Groth as correct and then the birefringence in the plate from both sets of values† by applying the formula

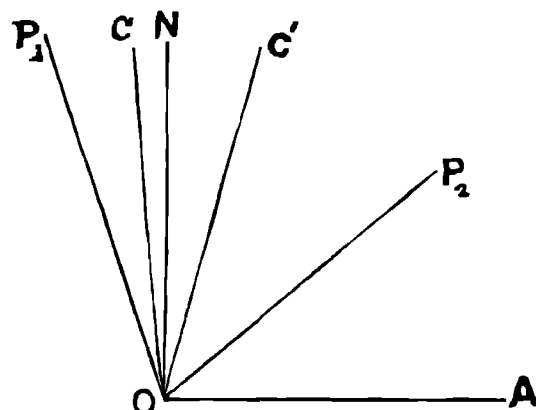
$$\frac{1}{a'^2} - \frac{1}{\gamma'^2} = \left(\frac{1}{a^2} - \frac{1}{\gamma^2} \right) \sin \theta \sin \theta'$$

where a' and γ' denote the principal indices in the plate the normal to which makes the real angles θ and θ' with the optic axes and a and γ denote the minimum and maximum principal refractive indices of the crystal

$a' - \gamma'$ has come out according to Narasimham's set of values as .024 and according to those of Hendricks and Jefferson as .0712. The latter is in satisfactory agreement with the author's observations and hence Hendricks and Jefferson's values are taken as reliable.

We proceed now to fix the orientations of the principal optic axes. The true angles θ and θ' are (from Hendricks and Jefferson's refractive indices and Groth's apparent angles) $18^{\circ} \cdot 56'$ and $50^{\circ} \cdot 48'$. Hence the acute bisectrix which in this case is the direction of maximum refractive index can easily be seen with the aid of the figure to make an angle of $20^{\circ} \cdot 42'$ with the crystallographic C axis in the obtuse angle

† In the case of values given by Hendricks and Jefferson the maximum refractive index is put equal to 1.90



OA=A axis, OP_2 =Optic axis, OC' =Bisectrix, ON =Normal, OC =C axis, OP_1 =Optic axis; $\angle COA=91^\circ 46'$; $\angle P_1ON=18^\circ 50'$; $\angle P_2ON=50^\circ 18'$, $\angle C'OC'=20^\circ 42'$.

This indeed coincides with the minimum diamagnetic axis and hence the direction in which the length of the molecule lies. Thus it appears that the optics of a suitable monoclinic crystal will enable us to fix the direction of the length of the molecule along which we naturally expect the maximum optical polarisability to occur. Unfortunately the data on the optics of organic crystals are very meagre and where available not quite reliable and so we cannot extend such investigations to other cases.

We now calculate the optic moments b_1 , b_2 and b_3 of the diphenyl molecule from the known orientations which are represented in the scheme below and by making use of the formula which the author has derived in the previous paper (*loc cit.*) for the refractive indices in the principal directions. The values of p_1 , p_2 and p_3 are assumed to be 1.8, 2.8 and 8.0 same as those of naphthalene to which assumption we have been led by comparing the dimensions of the unit cell and the angle β in both cases. The density of the crystal is 1.154 (Ashutosh Mukherjee, 1933)

	X	Y	Z
1	0°	90°	90°
2	90°	31°	59°
3	90°	59°	31°

X, Y, Z are respectively the directions of maximum, intermediate and minimum refractive indices. 1, 2, 3 represent respectively the directions of the length, breadth and thickness of the molecule which are mutually at right

angles to one another $b_1 = 33.32 \times 10^{-24}$, $b_2 = 23.06 \times 10^{-24}$, $b_3 = 12.13 \times 10^{-24}$ c.g.s. units. From Krishnan, we have for the diamagnetic moments $a_1 = -1.1039 \times 10^{-28}$, $a_2 = -1.1039 \times 10^{-28}$ and $a_3 = -2.8828 \times 10^{-28}$ c.g.s. units

Substituting these values in the formula for C_V for the concentration for which observations have been made, the calculated value of C_M comes out as 4.3×10^{-13} against the observed value 4.0×10^{-13} in very close agreement

The refractive index of the solution can also be calculated by the aid of the formula

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1(b_1 + b_2 + b_3) + \nu_2(b_1' + b_2' + b_3')}{1 - \frac{1}{3}\nu_1(b_1p_1 + b_2p_2 + b_3p_3) - \frac{1}{3}\nu_2(b_1'p_1' + b_2'p_2' + b_3'p_3')}$$

which takes into account the anisotropy of the optical polarisation field. The calculated value comes out as 1.522 which is in fair agreement with the observed value 1.5084

(c) *Dibenzyl*—The magnetic birefringence of this substance has not been studied by the author as it was not available. We can, however, make use of the available data to discuss this case

The refractive indices of the crystal have been given by Hendricks and Jefferson as 1.7566, 1.6286 and 1.5292. The density of the crystal is 1.0738. The dimensions of the molecule are taken as 11, 11 and 3.8 A.U. ‡ for which the values of p_1 , p_2 , p_3 are calculated in the usual manner

$$p_1 = p_2 = 2.579 \text{ and } p_3 = 7.877$$

Groth's qualitative observations show that the direction of maximum refractive index lies at almost the same direction as the length of the molecule which Krishnan has fixed at an angle of $83^\circ.9$ to the C axis. By analogy with diphenyl, we make the assumption that it coincides with the direction

	X	Y	Z
1	0°	90°	90°
2	90°	30°	60°
3	90°	60°	30°

‡ See the diagram given by Dhar, *Ind. Jour. Phys.*, 1934, 9, 1.

of the length, and since b axis is by virtue of symmetry also the axis of intermediate refractive index, the principal directions of the crystal are easily fixed. The above is the scheme of orientations of the principal axes 1, 2, 3 of the molecule with respect to them.

The values of b_1 , b_2 , b_3 calculated come out as $b_1 = 32.36 \times 10^{-24}$, $b_2 = 28.74 \times 10^{-24}$ and $b_3 = 14.36 \times 10^{-24}$ c g s units

The observed refractive index of the liquid dibenzyl at a density of 0.942 grams per c c is given as 1.539 (*I C T*, Vol. I) which compares very favourably with 1.535 calculated from the formula

$$\frac{n^2 - 1}{4\pi\nu} = \frac{B_1 + B_2 + B_3}{3}$$

where

$$B_1 = b_1 \left(1 + p_1 \cdot \frac{n^2 - 1}{4\pi} \right)$$

Though this test on the optic moments is not unique, yet a comparison of these values with those of diphenyl shows that they are reliable

5. Conclusion

In conclusion we point out that the results obtained in the case of diphenyl are significant, showing how the optical properties of a crystal can be a useful check on the X-ray or magnetic analysis of molecular orientation when combined with the knowledge of the magnetic double-refraction, refractivity and depolarisation of the scattered light. At the same time, the validity of the various theories is put to the test. For instance, the theory of magnetic birefringence in regarding it as arising out of the orientation of optically and magnetically anisotropic molecules has found a direct verification in the phenomenon being connected with other independent phenomena, namely, the optical and magnetic anisotropy of crystals. Also the idea of anisotropic polarisation field has consistently been employed. The author's molecular theory of double-refraction of organic crystals has also been put to the test.

The author is highly thankful to Prof. Sir C. V. Raman, Kt., M.A., D.Sc., F.R.S., N.L., for having allowed the use of the strong electromagnet at the Indian Institute of Science, Bangalore, for making some of the observations contained in the present paper. He is also thankful to Mr. S. Bhagavantam for the many useful discussions which the author had with him on the subject. He takes this opportunity also to thank the syndicate of the Andhra University for having awarded him a Research Fellowship at the beginning of this academic year.

Summary

The results of observations made on the magnetic birefringence of organic solids dissolved in liquid carbon tetrachloride are given. The observed values of C_M for naphthalene solutions are compared with the value of C_M observed by Salceanu on molten naphthalene and found to be in good agreement. The principal optic axes of the diphenyl crystal are fixed on the basis of the author's own observations, those of Groth and also of Hendricks and Jefferson. The direction of maximum refractive index has been found to coincide with the direction which has been assigned to that of the length of the molecule by Krishnan from his diamagnetic observations on the crystal. The optic moments of diphenyl molecule are calculated from the refractive indices and are found to satisfy the observed magnetic birefringence and the refractive index of the solution. The optic moments of the dibenzyl molecule are similarly calculated from the refractive indices and found to agree with the observed refractive index of the liquid dibenzyl.

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VINOGRADOW'S SOLUTION OF WARING'S PROBLEM (II).

BY I. CHOWLA.

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(Communicated by Dr S Chowla)

IN the first part of this paper it was shown by the method of Vinogradov, as modified by Pillai, that

Theorem I If Hypothesis P^* is true, then for $n > n_0$, there exists a number w depending only on n such that every large number $\equiv 1 \pmod{w}$ can be expressed as a sum of $(3n + 2)$ "nth powers" ≥ 0

In the rest of this paper we shall suppose that $n > n_0$. The method of my first paper enables us to formulate the more general

Theorem II It is possible to find a number w depending only on n with the following property:

Let the sequence of positive integers ξ have the property that

$$\sum_{\substack{\xi \leq x \\ \xi \equiv 1 \pmod{w}}} 1 \gg x^{1-\epsilon}$$

for every positive ϵ . Then every large $N \equiv (2f + 1) \pmod{w}$ is expressible in the form

$$(x_1^n + x_2^n + \cdots + x_{n+2}^n) + (\xi_1 + \xi_2)$$

where ξ_1 and ξ_2 are numbers of the " ξ sequence" and the x 's are integers ≥ 0 .

The following special case is of interest:

Let the ξ sequence consist of the primes $\equiv 1 \pmod{w}$ not exceeding x . Then the property $\sum_{\substack{\xi \leq x \\ \xi \equiv 1 \pmod{w}}} 1 \gg x^{1-\epsilon}$ is true and hence (here $f = 1$):

Theorem III. There exists a number w depending only on n such that every large $N \equiv 3 \pmod{w}$ is expressible in the form

$$(x_1^n + x_2^n + \cdots + x_{n+2}^n) + (p_1 + p_2)$$

where the x 's are integers ≥ 0 and p_1, p_2 are primes.

* Hypothesis P is that $H_{n,n}(x) \gg x^{1-\epsilon}$ for any $\epsilon > 0$. Here $H_{n,n}(x)$ denotes the number of numbers $\leq x$ which can be expressed as a sum of n "nth powers" ≥ 0 . See the first part of this paper: *Proc Ind. Acad. Sci., (A)*, 1935, 2, 562-573.

THE RAMAN SPECTRA OF SOME ORGANIC LIQUIDS UNDER HIGH DISPERSION AND RESOLVING POWER.

(Benzene, Toluene, Phenol, Chlorobenzene, Pyridine and Cyclohexane.)

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(Communicated by Sir C. V. Raman, Kt, F.R.S., N.L.)

1 Introduction.

THE use of spectrographs of high dispersion and resolving power in the study of Raman spectra is obviously of great interest and importance from the point of view of the elucidation of the fine structure of some of the lines appearing in them, and the precision measurement of their wave-numbers. The chief difficulty in all such work is of course the extremely long duration of exposure required to get well-exposed photographs. Although this difficulty can be overcome to a certain extent by the use of high speed photographic plates and intense sources of illumination, the proper choice of the spectrograph is also an important matter for consideration. A new spectrograph which has been recently added to the Physics Laboratory of the Institute was found to be particularly suited for this type of work. It was therefore thought worth while to examine the Raman spectra of a few substances with this instrument.

2 Experimental.

The spectrograph was of Littrow model with glass optical parts, and was supplied by the firm of Adam Hilger Ltd. The prisms (one 60° and the other 30°) were of large size giving a resolving power of about 3 cm^{-1} in the region between $\lambda 1046$ and $\lambda 4358$. The dispersion in the region $\lambda 4358$ was about 10 \AA/mm . The instrument combined fairly good light gathering power with a high degree of optical perfection.

The experimental technique was the same as that described by the author on a previous occasion,¹ the quartz mercury arc being put in direct contact with a water mantle enveloping the Raman tube with concave metallic reflectors above and below. The slit width in all experiments was 50μ as it was found that further diminution of it failed to bring out any additional spectral details (so far as the present work was concerned), and resulted only

¹ R. Ananthakrishnan, *Proc. Ind. Acad. Sci., A*, 1935, **2**, 452.

in a general loss of intensity necessitating longer exposures. The illumination was so powerful, and the experimental conditions so good that a very intense spectrum of benzene could be obtained in 24 hours. Longer exposures did not reveal any additional features. Ilford golden isozenith plates with special backing were employed for photographing the spectra; an iron arc comparison spectrum was photographed at the centre of the Raman spectrum on all the plates.

3 Results

The plates were measured on a Hilger Cross-slide micrometer and the frequency shifts of the Raman lines were determined using linear interpolation from the nearest iron arc lines. In the case of sharp lines the results are correct to $\pm 1 \text{ cm}^{-1}$. The 992 line of benzene and its satellites were measured several times with the greatest care, and the results in this case are probably correct to $\pm 0.5 \text{ cm}^{-1}$. The complete classification of the spectra of the substances studied in the interval between $\lambda 4046$ and $\lambda 5100$ is given at the end of the paper. (Tables I to VI.)

(1) *Benzene* — The Raman spectrum of this substance has formed the subject of investigation by several workers from diverse standpoints. The complete literature on the subject would be too lengthy, and reference may be made to Sirkar's bibliography of the Raman effect². We may mention in particular the careful work of Dr. Krishnamurti,³ and the more recent and elaborate investigation of Grassmann and Weiler.⁴ The latter authors have reported many new lines of feeble intensity, all of which, however, could not be confirmed in the present work, probably because of the lack of sensitivity of the plates employed in the spectral regions concerned. In Table VII we have given our results side by side with those of the above-mentioned authors. The infra-red absorption frequencies in the last column are taken from Coblentz's book. A surprisingly close coincidence is noticed between the Raman and infra-red frequencies, but whether this coincidence is one of principle or merely accidental is a disputed point.

Placzek⁵ has pointed out that the interpretation of the benzene spectrum is confronted with great difficulties. If we take the plane regular hexagonal model of the benzene molecule, then it follows from symmetry considerations that all Raman frequencies should be inactive in the infra-red and *vice versa*.

² S. C. Sirkar, *Ind. Jour. Phys.*, 1932, 7, 431, S. C. Sirkar and D. Chakravarty, *Ind. Jour. Phys.*, 1935, 9, 553.

³ P. Krishnamurti, *Ind. Jour. Phys.*, 1931, 6, 543.

⁴ P. Grassmann and J. Weiler, *Z. f. Phys.*, 1933, 86, 321.

⁵ G. Placzek, *Leipziger Vorträge*, 1931, S 71.

E. B. Wilson,⁶ however, has expressed the view that in so far as infra-red data are lacking in precision, the coincidence of Raman and infra-red frequencies cannot be asserted with certainty "to establish a result contrary to all other evidence".

The normal vibrations of the benzene molecule have been worked out by E. B. Wilson⁷ who has ascribed to it twenty distinct fundamental frequencies. Of these, seven are Raman-active, four infra-red-active, while the nine remaining fundamentals are completely inactive. Wilson's assignment of the fundamental frequencies⁸ is as given below. —

Raman-active		Infra-red-active
$\nu_1 = 991 \text{ cm.}^{-1}$	$\nu_7 = 3047$	$\nu_{11} = 1040 \text{ cm.}^{-1}$
$\nu_2 = 3060$	$\nu_8 = (1584-1605)$	$\nu_{18} = 660$
$\nu_6 = 605$	$\nu_9 = 849$	$\nu_{10} = 1480$
	$\nu_{10} = 1178$	$\nu_{20} = 3080$

"The remaining lines and bands which are nearly all much weaker than those assigned to fundamentals are to be considered as overtones and combinations from this viewpoint." It might be remarked that the classification does not account for the strong infra-red absorption frequency at 1183 whose coincidence with the Raman frequency 1178 has been pointed out by Dr. Placzek⁹ as a result incompatible with the usually accepted plane model of the benzene ring with a centre of symmetry. Similarly, the origin of the Raman line at 2949 cm.^{-1} which is perhaps stronger than the line at 1178 is also not quite clear. As has been pointed out by Grassmann and Weiler,¹⁰ it might probably be the octave of the strong infra-red absorption frequency 1480. The strange coincidence of the Raman frequency 2949 of benzene with the C-H frequency observed in the case of aliphatics, as well as its disappearance in the monosubstituted benzene derivatives, has, however, been a great puzzle.¹¹

⁶ E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

⁷ E. B. Wilson, *Phys. Rev.*, 1934, **45**, 706.

⁸ E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

⁹ G. Placzek, *Quantenmechanik der Materie und Strahlung*, Teil II, S. 235.

¹⁰ P. Grassmann and J. Weiler, *Loc. cit.*

¹¹ See K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, p. 225.

According to Wilson,¹² the doublet at 1600 cm^{-1} in the Raman spectrum of benzene is to be explained on the basis of quantum-mechanical resonance (as in the case of CCl_4) because the sum $\nu_1 + \nu_8 = 1596\text{ cm}^{-1}$ falls between the members of the doublet ν_8 . He has also pointed out that additional evidence in support of this view is provided by the Raman spectra of benzene derivatives "In nearly all of these a single line occurs near 1600 cm^{-1} , in none of them is a doublet reported". This is in harmony with the fact that the accidental degeneracy $\nu_1 + \nu_8 \sim \nu_8$ is not nearly so close as in benzene." The above statement appears to have been made from an insufficient knowledge of the experimental data. To illustrate this point, we give below the following table:—

Substance	Frequencies and relative intensities		
C_6H_6	606 (5)	992.5 (10)	1584 (3), 1605 (2)
$\text{C}_6\text{H}_5\text{CH}_3$	622 (4b)	1005 (10s)	1588 (2), 1606 (3), 1630 (0)
$\text{C}_6\text{H}_5\text{Cl}$	615 (3)	1003 (10s)	1565 (0), 1581 (4)
$\text{C}_6\text{H}_5\text{OH}$	620 (4)	1001 (10)	1595 (5), 1605 (5)
$\text{C}_5\text{H}_5\text{N}$	602 (1)	990 (10)	1570 (2), 1579 (2), 1594 (1)

The structure of the benzene molecule has been the theme of a recent note in *Nature* by Angus, Bailey, Ingold, Leckie, Raisin, Thompson and Wilson¹³ who have investigated the Raman and infra-red spectra of hexadeutero-benzene. Coincident frequencies are found in this case also, though not so many as in the case of benzene. These authors therefore believe that these are not coincidences of principle, but are accidental, and come to the conclusion that no real objection remains against the usually accepted structure of the benzene molecule.

Further discussion of the Raman spectrum of benzene is postponed to the next section.

(2) *Toluene*—The Raman spectrum of this substance has been studied under high dispersion by Howlett¹⁴ and also by Mesnage¹⁵. More recently,

¹² E. B. Wilson, *Phys. Rev.*, 1934, **46**, 146.

¹³ W. R. Angus, C. R. Bailey, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson and C. L. Wilson, *Nature*, 1935, **136**, 680.

¹⁴ L. E. Howlett, *Canad. Jour. Res.*, 1931, **5**, 572.

¹⁵ P. L. Mesnage, *Jour. de Phys.*, 1931, **2**, 403.

Kohlrausch¹⁶ has made a systematic reinvestigation of the Raman spectra of benzene derivatives. The Raman frequencies are given in Table VIII. The infra-red absorption maxima are given in the last column. Here again, we find many frequencies common to the Raman and infra-red absorption spectra. A number of new Raman lines have been found in the region between $\Delta\nu = 1200$ and 1500 cm^{-1} , some of which correspond to the infra-red frequencies present in this interval.

(3) *Phenol*.—The Raman frequencies of this substance obtained in the present investigation are given along with those reported by Kohlrausch¹⁷ in Table IX. Several new frequencies have been found, and some of the lines previously reported as broad have been found to be doublets: *e g*, 1162 (5*b*), 1599 (7*b*), and 3060 (12*b*). The broad diffuse band at 3524 cm^{-1} , also reported by Kohlrausch is to be attributed to the O-H oscillation.

(4) *Chlorobenzene*—Murray and Andrews¹⁸ have made a detailed study of the Raman spectrum of $\text{C}_6\text{H}_5\text{Cl}$ and have reported several new lines. Many of these are confirmed by the present work. The Raman frequencies and infra-red absorption maxima are given in Table X.

(5) *Pyridine*—Krishnamurti¹⁹ has made a detailed study of the Raman spectrum of pyridine and has reported several new frequencies. Very recently Kohlrausch and Pongratz²⁰ have studied the Raman spectrum of this substance. Unfortunately, the latter authors have overlooked the work of Krishnamurti, so that not only those frequencies which they report as new, but several other frequencies not obtained by them are contained in Krishnamurti's paper. The present work confirms almost all the frequencies reported by Krishnamurti and also shows that some of these frequencies are actually doublets. The results are given in Table XI. The remarkable coincidence between the Raman and infra-red absorption frequencies may be seen from the table.

(6) *Cyclohexane*—A careful investigation of the Raman spectrum of this substance has been made by Krishnamurti²¹ whose results along with those of the author are given in Table XII. The line $\Delta\nu = 992$ (0) arises most probably from a trace of benzene impurity. The line $\Delta\nu = 695$ (0) reported by Krishnamurti is not confirmed as the corresponding line is not

¹⁶ K. W. F. Kohlrausch and A. Pongratz, *Sitz. der Kais. Acad. Wiss.*, 1933, **142**, 637.

¹⁷ K. W. F. Kohlrausch and A. Pongratz, *Loc. cit.*

¹⁸ J. M. Murray and D. H. Andrews, *Jour. Chem. Phys.*, 1933, **1**, 402.

¹⁹ P. Krishnamurti, *Ind. Jour. Phys.*, 1931, **6**, 543.

²⁰ K. W. F. Kohlrausch and A. Pongratz, *Ber. der Deut. Chem. Ges.*, 1934, **67**, 1465.

²¹ P. Krishnamurti, *Ind. Jour. Phys.*, 1931, **6**, 543.

observed by 4046 excitation. It would seem that the line in question is really the 802 line excited by λ 4339 and not 695 coming from λ 4358. Between $\Delta\nu = 2852$ – 2922 cm^{-1} Krishnamurti has reported a continuous background and a line at 2889. In the present work three lines 2870, 2888 and 2898 are observed in this region.

4 The Carbon Isotope and the Fine Structure of the 992 Line of Benzene.

The fine structure of the Raman line 992 cm^{-1} of benzene has been investigated by Weiler,²² Howlett,²³ Mesnage,²⁴ L. and E. Bloch,²⁵ Grassmann and Weiler,²⁶ Specchia and Scandurra²⁷ and more recently by Bhagavantam²⁸. The following table gives a collective summary of the results of various investigators.—

Author	Frequencies and Relative Intensities				
J. Weiler (1931)	982 (1)	992.0 (4)			
L. E. Howlett (1931)	980.3 (5)	983.9 (5)	992.2 (10)	998.5 (5)	1005.3 (0)
P. L. Mesnage (1931)	981.2 (2)	992.4 (10)			
L. and E. Bloch (1933)	978.5 (0)	983.8 (2)	992.2 (20)	999.0 (1)	1006.0 (0)
P. Grassmann and J. Weiler (1933)	979 (1)	984 (2)	992.5 (15)	(999)	1005 (1)
O. Specchia and G. Scandurra (1935)	977	984	992	1002	
S. Bhagavantam (1935)		985 (1)	992.2 (20)		
R. Ananthakrishnan (1935)	979 ($\frac{1}{2}$)	984(1)	992.5 (10)	998 (1)	1006 ($\frac{1}{2}$)

A little consideration will show that the results of the different workers are not really discordant except in so far as the visual estimates of the relative intensities are concerned. The latter remark applies especially to

²² J. Weiler, *Z. f. Phys.*, 1931, **69**, 586.

²³ L. E. Howlett, *Loc. cit.*

²⁴ P. L. Mesnage, *Loc. cit.*

²⁵ L. and E. Bloch, *C. R.*, 1933, **196**, 1787.

²⁶ P. Grassmann and J. Weiler, *Loc. cit.*

²⁷ O. Specchia and G. Scandurra, *N. Cimento*, 1935, **12**, 129.

²⁸ S. Bhagavantam, *Proc. Ind. Acad. Sci. A*, 1935, **2**, 86.

Howlett's intensity estimates of the satellites which are certainly far too high. As regards the frequencies themselves, it might be pointed out that 982 and 981.2 reported by Weiler and Mesnage respectively may be regarded as the mean of the two frequencies 979 and 984, the separation being not observed by them, probably on account of the insufficient resolving power of the instruments employed. The 1002 lines reported by Specchia and Scandurra is perhaps the mean of 998 and 1006. The line at 998 cm^{-1} is just resolved from the main line at 992.5 and appears as a wing to the latter. Such a wing to the total symmetric vibration Raman line of CCl_4 has been recently reported by the author²⁹. A microphotometric study of the intensity distribution in the wing in these two cases would appear to be of great interest in view of the recent work of Bhagavantam, Weiler and others on the distribution of intensity in the rotational wings accompanying the Rayleigh line in the case of liquids.

The author's findings regarding the fine structure of the 992 line of benzene stands in good agreement with that of Grassmann and Weiler, L. E. Howlett and L. and E. Bloch. In view of this, the remark of Bhagavantam³⁰ that "the failure to record the other components, *viz.*, 980.3, 999, etc., in the present investigation is very significant..... A possible explanation is that they have arisen from traces of impurities such as toluene, etc., " does not seem to be justified. The fact that Bhagavantam could record only the strongest satellite was probably because either the duration of exposure or the resolving power of the instrument employed was insufficient.

As is well known, the Raman line 992.5 cm^{-1} in the case of benzene, corresponds to the symmetrical expansion and contraction of the benzene ring. Following the original suggestion of Gerlach,³¹ Grassmann and Weiler, Specchia and Scandurra, and Bhagavantam have attributed the strong satellite at 984 cm^{-1} to the vibration of the benzene nucleus in which one of the six carbon atoms is the heavier isotope C_{13} . The satellites of lesser intensity are, in the opinion of Grassmann and Weiler, to be interpreted as combination tones. In order to investigate the matter more thoroughly, these authors undertook polarisation measurements and found that the satellite at 984 is polarised to the same extent as the principal line at 992.5. However, they were unable to draw any conclusions as regards the state of polarisation of the other satellites since these could not be recorded in the polarisation experiments on account of their feeble intensity.

²⁹ R. Ananthakrishnan, *Loc cit*

³⁰ S. Bhagavantam, *Loc cit*.

³¹ W. Gerlach, *Ber. d. Bayr. Akad. d. Wiss.*, 1932, 1, 39

Following Bhagavantam, we can calculate to a first order of approximation the change in frequency that would be produced if one of the six carbon atoms of the benzene nucleus were to be replaced by the isotope C_{13} . If the symmetrical expansion of the benzene ring C_6^{12} has got the frequency 992.5, the corresponding frequency for the ring $C_5^{12}C^{13}$ works out easily as 986, provided it be assumed that the introduction of the heavier isotope does not appreciably affect the symmetry character of the ring. The deviation between the observed frequency 984 and the calculated frequency 986 appears to be too great to attribute it to an error in measurement.

The abundance ratio of the carbon isotopes C^{12} and C^{13} as given by different workers is very divergent. The recent estimate of Aston³² gives the most probable value ratio of abundance as $C^{13} : C^{12} \dots 1 : (110 \pm 14)$. As Bhagavantam has pointed out, this ratio gives for the expected satellite an intensity which is roughly 1/23rd of the intensity of the main line. Although too much emphasis cannot be laid on visual estimates of intensity, it appears from the photographs that the relative intensity of the satellite at 984 is greater than this value.

We shall now consider a little more closely the Raman spectra of the monosubstituted derivatives of benzene. It is well known that a number of the Raman lines of benzene occur also in its monoderivatives with practically the same frequency and degree of depolarisation. These frequencies have therefore their origin presumably in the vibrations of the carbon ring. In the case of benzene these frequencies have the following values

$\Delta\nu = 606, 992, 1176, 1600$ (double) and 3060 (double). Of these $\Delta\nu = 992 \text{ cm}^{-1}$ is of special interest for reasons already pointed out. In the monoderivatives of benzene the corresponding line has a slightly higher

Substance	Frequency and Relative Intensities				
C_6H_6	979 ($\frac{1}{2}$)	984 (1)	992.5 (10)	998 (1) (wing)	1006 ($\frac{1}{2}$)
$C_6H_5CH_3$	978 ($\frac{1}{2}$)		993 ($\frac{1}{2}$)		1005 (10)
C_6H_5Cl		989 (0)		1003 (1)	1013 (00)
C_6H_5ON		991 (00)		1001 (10)	1013 (0) (wing)
C_5H_5N	979 (0)	990 (10)			

³² F. W. Aston, *Proc. Roy. Soc., A*, 1935, **149**, 396

frequency, and the present investigation shows that in all cases it is accompanied by faint satellites.

The faint companion to the shorter wave-length side of the strong line is in all cases very sharp but its frequency and relative intensity do not seem to bear any simple relation to those of the main line. Its relative intensity is greatest in the case of toluene and least in the case of phenol.

Structure of the Raman line 802 cm^{-1} of cyclohexane.—As in the case of the $992\cdot5$ line of benzene, the 802 line of cyclohexane represents the frequency of the symmetric expansion and contraction of the puckered carbon ring which forms the nucleus of this molecule. Bhagavantam³³ has reported an "unresolved blackening" to the shorter wave-length side of this line, which, however, is not confirmed by the present work. It seems desirable to point out the remarkable dissimilarity in the structure of the Raman line corresponding to the symmetrical vibration in the case of benzene and cyclohexane. An enlargement of these two lines excited by $\lambda\ 4047$ is reproduced in the Plate. The 802 line of cyclohexane is quite sharp and is completely free from wings and satellites. If the satellite at 984 cm^{-1} in the case of benzene is to be attributed to the nucleus $\text{C}_6^{12}\text{C}^{13}$, we ought to expect a similar satellite with the same relative intensity and a frequency shift of $796\cdot7\text{ cm}^{-1}$ in the case of cyclohexane. The fact that there is not even the faintest trace of such a satellite, when taken together with other difficulties already pointed out, renders it highly improbable that the 984 satellite of benzene has its origin in the carbon isotope.

5. Conclusion.

The present investigation shows that there exists a fundamental difference between the structure of the 992 line of benzene and the corresponding line in the case of its monosubstituted derivatives. How far it is correct to interpret the satellites of the $992\cdot5$ line of benzene as well as many of the less intense lines in its Raman spectrum as over- and combinational tones remains an open question. That the benzene problem is beset with several difficulties has been already emphasised. It may be that many of these difficulties as well as the fine structure of the 992 line itself are all intimately connected with the constitution of the benzene ring which is still a problem not completely understood.

The author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest and suggestions in the course of the present work.

³³ S. Bhagavantam, *Loc. cit.*

Summary.

A detailed study of the Raman spectra of benzene, toluene, phenol, chlorobenzene, pyridine and cyclohexane has been made with a spectrograph of high dispersion and resolving power. Several faint lines have been observed in the Raman spectra of these substances many of which agree with those reported by previous workers, and some of which are reported for the first time. The Raman spectrum of phenol in particular shows several new features. A careful study has been made of the fine structure of the 992 line of benzene, and it is found to consist of four satellites in addition to the main line at 992.5 cm^{-1} . The frequencies and relative intensities are: 979 ($\frac{1}{2}$), 984 (1), 992.5 (10), 998 (1), 1006 ($\frac{1}{2}$). The corresponding Raman line (802 cm^{-1}) in the case of cyclohexane shows no fine structure. The possibility of the 984 satellite of benzene arising from the carbon isotope C^{13} has been discussed, and several difficulties are pointed out which render it difficult to attribute such an origin to this satellite. The study of the Raman spectrum of the monoderivatives as well as of pyridine shows that the intense Raman line which corresponds to the symmetrical expansion and contraction of the nucleus is in all cases accompanied by a faint companion to the shorter wave-length side. The frequency and relative intensity of this satellite, however, seem to bear no unique relation to those of the main line. It is concluded that the peculiar structure of the 992 line of benzene is probably connected with the constitution of the benzene ring.

Note on chemicals—The benzene employed in the present work was the "Kahlbaum" variety for the determination of molecular weight. No special purification was therefore considered necessary excepting the usual process of vacuum distillation to remove suspended notes. Toluene, pyridine and chlorobenzene were subjected to preliminary fractionation in a rectifying column, and the middle fractions distilling at constant boiling point were used in the experiment. Phenol was available in the pure crystalline state, while cyclohexane was taken from a bottle labelled "pure" and supplied by the firm of Theodor Schucardt.

The duration of exposure varied from 24 hours in the case of benzene and chlorobenzene to 48 hours in the case of toluene, pyridine and phenol. Cyclohexane gave a very clear and intense Raman spectrum with a continuous exposure of 80 hours. It may be interesting to add that phenol was a supercooled liquid at 25°C . during the time of exposure.

The notation employed in the accompanying Tables is as follows and is taken from Kohlrausch's well-known book:—

Exciting line Å	Notation	Wave Number (cm. ⁻¹)
4358.34	<i>e</i>	22938
4347.50	<i>f</i>	22995
4339.24	<i>g</i>	23039
4108	<i>h</i>	24335
4077.81	<i>i</i>	24516
4046.56	<i>k</i>	24705.1
3981	<i>l</i>	25098
3906	<i>m</i>	25592
3663	<i>o</i>	27293
3655	<i>p</i>	27353
3650	<i>q</i>	27388

Diffuse lines of zero intensity whose assignments are not quite certain are indicated by an interrogation mark. An asterisk against some of the frequencies indicates that the corresponding lines show a doublet structure.

The abbreviations employed in the Tables have the following significance —

s = sharp, *b* = broad, *d* = diffuse; *vb* = very broad.

Anti-stokes lines are indicated by a bar placed over the corresponding frequencies.

TABLE I Raman Spectrum of Benzene

No.	ν	Int.	Assignment	No	ν	Int	Assignment
1	19874	3	$e-3061$	37	22535	1d	$\left\{ \begin{array}{l} e-403 \\ m-3057 \end{array} \right.$
2	19890	1	$e-3048$	38	23100	2	$k-1605$
3	19988	0	$e-2950$	39	23121	3	$k-1584$
4	21333	2	$\left\{ \begin{array}{l} e-1605 \\ i-3188 \end{array} \right.$	40	23230	0	$k-1175$
5	21353	3	$\left\{ \begin{array}{l} e-1585 \\ i-3167 \end{array} \right.$	41	23260	0	$k-1115$
6	21392	0	$f-1603$	42	23302	$\frac{1}{2}d$	$k-1103$
7	21412	0	$f-1583$	43	23341	1d	$\left\{ \begin{array}{l} h-992 \\ i-1175 \end{array} \right.$
8	21454	3	$\left\{ \begin{array}{l} e-1481 \\ i-3062 \end{array} \right.$	44	23383	0d	$o-3910?$
9	21468	$\frac{1}{2}$	$i-3041$	45	23435	0d	$p-3918?$
10	21493	00	$e-1445$	46	23180	0d	$q-3908?$
11	21518	1	$k-3187$	47	23523.5	6	$i-992.5$
12	21541	$\frac{1}{2}$	$\left\{ \begin{array}{l} e-1397 \\ k-3161 \end{array} \right.$	48	23532	2	$\left\{ \begin{array}{l} i-934 \\ k-1173 \end{array} \right.$
13	21566	$\frac{1}{2}$	$i-2950$	49	23544	$\frac{1}{2}$	$e-606$
14	21589	00	$i-2927$	50	23670	$\frac{1}{2}$	$\left\{ \begin{array}{l} i-846 \\ k-1035 \end{array} \right.$
15	21642	8	$k-3063$	51	23699.4	$\frac{1}{2}$	$k-1006$
16	21657	4	$k-3048$	52	23707.6	2	$k-997.8$
17	21756	5	$k-2949$	53	23712.6	15	$k-992.8$
18	21762	2	$e-1176$	54	23721.4	2	$k-984$
19	21777	0bd	$k-2928$	55	23726	1	$k-979.4$
20	21820	0	$f-1175$	56	23855	1d	$k-850$
21	21862	00	$g-1177$	57	23905	$\frac{1}{2}$	$k-800$
22	21904	0	$e-1034$	58	23930	1	$\left\{ \begin{array}{l} e-992 \\ k-775 \end{array} \right.$
23	21933	0	$e-1005$	59	24009	00d	$k-686$
24	21945.2	10	$e-992.8$	60	24099	5b	$\left\{ \begin{array}{l} k-606 \\ o-3194 \end{array} \right.$
25	21954	1	$e-984$	61	24125	1d	$o-3168$
26	21959	0	$e-979$	62	24165	2	$p-3188$
27	22003.5	3	$f-991.8$	63	24185	0	$p-3168$
28	22047	2	$g-992$	64	24201	4	$q-3187$
29	22088*	2	$\left\{ \begin{array}{l} e-850 \\ k-2617 \end{array} \right.$	65	24228	6b	$\left\{ \begin{array}{l} o-3065 \\ q-3160 \end{array} \right.$
30	22136	0	$e-802$	66	24242	1	$o-3051$
31	22158	$\frac{1}{2}$	$\left\{ \begin{array}{l} e-780 \\ k-2547 \end{array} \right.$	67	24286	8	$p-3067$
32	22248*	$\frac{1}{2}$	$\left\{ \begin{array}{l} e-690 \\ k-2457 \end{array} \right.$	68	24305	1	$\left\{ \begin{array}{l} k-400 \\ p-3048 \end{array} \right.$
33	22331	5	$e-607$	69	24325	9	$q-3063$
34	22388	0	$f-607$	70	24344	4d	$o-2949$
35	22413	0	$k-2292$	71	24404	3	$p-2949$
36	22438	0	$g-601$	72	24438	5	$q-2950$

402(1d), 606(5), 688($\frac{1}{2}$), 778(0), 801(0), 850(2), 979($\frac{1}{2}$), 984(1), 992.5(10), 998(1), 1006($\frac{1}{2}$), 1035(0), 1175(2), 1400($\frac{1}{2}$), 1445(0), 1480(0), 1584(3), 1605(2), 2292(0), 2457($\frac{1}{2}$), 2547($\frac{1}{2}$), 2617(0), 2928(0d), 2949(5), 3048(4), 3064(8), 3164($\frac{1}{2}$), 3187(1), (3910)(0d).

TABLE II
Raman Spectrum of Toluene

No	ν	Int	Assignment	No.	ν	Int.	Assignment
1	19980	3b	e-3058	46	23206	0	k-1499
2	20018	2	e-2920	47	23250	0d	k-1455
3	21315	0	e-1623	48	23272	0d	k-1433
4	21331	3	e-1007	49	23304	1s	i-1213
5	21350	2	e-1588				k-1401
6	21387	00	f-1608	50	23324	3	k-1381
7	21406	00	f-1599	51	23357	0d	i-1159
8	21460	2b	i-3056	52	23390	0d	k-1315
9	21484	0	e-1454	53	23423	0d	k-1282
10	21503	0	e-1435	54	23457	1	e-519
11	21534	$\frac{1}{2}s$	c-1404	55	23485	1	i-1031
12	21555	2s	e-1383	56	23494	6s	k-1211
13	21597	$\frac{1}{2}b$	i-2919	57	23510	4s	i-1006
14	21634	6b	k-3071	58	23524	1	k-1181
15	21645	8	k-3060	59	23548	2	k-1157
16	21668	4b	k-3037	60	23672	8s	k-1033
17	21703	$\frac{1}{2}$	k-3002	61	23699	10s	k-1006
18	21725	6s	e-1213	62	23711	$\frac{1}{2}s$	k-993
19	21750	1	e-1182	63	23722	0	e-784
20	21783	6b	(e-1155 k-2922)	64	23728	1	(i-788 k-977)
21	21837	3 vb	k-2868	65	23811	0b	k-894
22	21909	8s	e-1029	66	23865	0b	k-840
23	21933	10s	e-1005	67	23805	0b	(i-021 k-810)
24	21945	$\frac{1}{2}s$	e-993	68	23917	10s	k-788
25	21960	$\frac{1}{2}$	e-978	69	23941	0	e-1003
26	21968	0	f-1027	70	23969	0	e-1031
27	21989	$\frac{1}{2}s$	f-1006	71	23975	0	k-730
28	22009	00	q-1030	72	23993	$\frac{1}{2}s$	i-523
29	22034	0	q-1005	73	24084	4b	k-621
30	22040	0b	e-898	74	24124	0b	k-581 ²
31	22095	0b	e-843	75	24182	6s	k-523
32	22122	0b	e-816	76	24220	3	o-3073
33	22150	9s	e-788	77	24234	6	o-3059
34	22205	$\frac{1}{2}$	(e-733 f-790)	78	24255	1d	o-3038
35	22250	0	g-789	79	24284	4	p-3069
36	22314	3	e-624	80	24296	6	p-3057
37	22415	5	e-523	81	24139	5b	(q-3069 o-3034)
38	22470	$\frac{1}{2}$	f-525				(q-3038 p-3003)
39	22537	0 vb	m-3055	82	24350	4b	o-2933
40	22604	$\frac{1}{2}$	e-334	83	24370	4b	q-3006
41	22670	0	m-2922	84	24382	$\frac{1}{2}$	p-2924
42	22720	6b	e-218	85	24429	6b	q-2933
43	23099	3	k-1606	86	24465	6b	
44	23118	1	k-1587				
45	23153	1b	e-215				

218 (6b), 334 ($\frac{1}{2}$), 523 (5), (581) (0), 622 (4b), 730 (0), 788 (10), 813 (0b), 842 (0b), 896 (0b), 978 ($\frac{1}{2}$), 993 ($\frac{1}{2}$), 1005 (10s), 1030 (8s), 1157 (2), 1181 (1), 1212 (6s), 1282 (0), 1315 (0), 1348 (0), 1381 (2), 1402 (0), 1434 (0), 1455 (0), 1499 (0), 1588 (2), 1606 (3), 1630 (0), 2868 (3**vb**), 2922 (6b), 3002 ($\frac{1}{2}$), 3037 (4b), 3058 (8), 3070 (6b).

TABLE III.
Raman Spectrum of Phenol

No	ν	Int	Assignment	No	ν	Int	Assignment
1	19879	3b	c—3059	40	22530	0bd	m—3062
2	21171	0bd	k—3524	41	22696	5b	e—242
3	21332	5	e—1606	42	23100	5	k—1605
4	21342	5	e—1596	43	23111	5	l—1594
5	21394*	00b	f—1601	44	23179	2b	e—241
6	21441	$\frac{1}{2}$	e—1497	45	23206	0	k—1499
7	21455	2b	i—3061	46	23241	0	k—1464
8	21505	0bd	k—3200	47	23280	00	k—1425
9	21555	00d	k—3150	48	23345	0	i—1171
10	21620*	$\frac{1}{2}$	k—3085	49	23360	0	i—1156
		(wing)		50	23449	2b	k—1256
11	21641	8	k—3064	51	23473	0	e—595
12	21654	5	k—3051	52	23490	1	i—1026
13	21688	2b	e—1250	53	23515	3	i—1001
14	21714	$\frac{1}{2}$ b	l—3017	54	23535	3	l—1170
15	21740	00b	f—1255	55	23550	3	k—1155
16	21768	4s	e—1170	56	23592	0	k—1113
17	21784	3s	e—1154	57	23634	1	k—1071
18	21825	0	(e—1113) (f—1170)	58	23678	8	k—1027
19	21840	00	(f—1155)	59	23693	0	(e—755 k—1012)
20	21866	1s	e—1072			(wing)	
21	21911	8s	e—1027	60	23704	10	k—1001
22	21923	0	e—1015	61	23715	00	k—990
		(wing)		62	23751	0	e—816
23	21937	10	e—1001	63	23766	00	i—750
24	21947	00	e—991	64	23830	0bd	p—3520
25	21968	0	f—1027				i—623
26	21994	$\frac{1}{2}$ s	f—1001	65	23877	3	(k—828 l—812)
27	22040	0	q—999	66	23893	8	l—812
28	22107	4	e—831	67	23918	0b	k—787
29	22125	8	e—813	68	23950	2b	k—755
30	22153	0d	e—785	69	23982	$\frac{1}{2}$	i—534
31	22181	3b	(e—757 f—814)	70	24000	00d	k—705
32	22227	00d	q—812	71	24085	4	k—620
33	22273	00d	e—665	72	24114	0d	k—591
34	22319	5s	e—619	73	24171	4b	k—534
35	22349	00	e—589	74	24199	1	k—506
36	22377	00	f—618	75	24230	4b	o—3063
37	22407	4	e—531	76	24270	$\frac{1}{2}$	i—246
38	22430	1	e—508	77	24289	6b	p—3062
39	22460	0	f—530	78	24324	6	q—3064
				79	24462	4b	k—243

243 (5b), 507 ($\frac{1}{2}$), 532 (4), 590 (0), 620 (4), 655 (00d), 756 (3), 787 (0b), 812 (8), 830 (3), 991 (0), 1001 (10), 1013 (0), 1027 (8s), 1072 (1), (1113) (0), 1155 (3s), 1170 (4s), 1253 (2b), (1425) (00), 1464 (0), 1498 ($\frac{1}{2}$), 1595 (5), 1605 (5), 3017 ($\frac{1}{2}$ b), 3051 (5), 3064 (8), 3035 ($\frac{1}{2}$) (3150) (00d), 3200 (0bd), 3524 (0rb)

TABLE IV
Raman Spectrum of Chlorobenzene.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19870	2b	e—3066	38	23336	0	k—1369
2	21353	3	e—1585	39	23358	1	e—440
3	21373	0	e—1565	40	23384	0	k—1321
4	21413	00	f—1582	41	23410	0	k—1295?
5	21448	2	e—3068	42	23435	$\frac{1}{2}$	i—1081
6	21492	0	e—1446	43	23493	1s	i—1023
7	21542	1	k—3163	44	23514	2s	i—1002
8	21564	0	{ e—1374 k—3141	45	23531	$\frac{1}{2}$	k—1174
9	21616	0	e—1322	46	23548	1	k—1157
10	21637	10b	k—3068	47	23585	$\frac{1}{2}$	k—1120
11	21677	0	k—3028	48	23622	5	k—1083
12	21697	0	k—3008	49	23638	0	e—700
13	21760	0	e—1178	50	23681	8	k—1024
14	21780	$\frac{1}{2}$	e—1158	51	23692	00	k—1013
15	21815	0	e—1123	52	23702	10s	k—1003
16	21853	4	e—1085	53	23715	0s	k—990
17	21914	6s	e—1024	54	23780	0	k—925
18	21925	00	e—1013	55	23815	$\frac{1}{2}$	i—701
19	21935	10s	e—1003	56	23874	0	k—831
20	21949	0s	e—989	57	23901	0	i—612
21	21971	0s	f—1024	58	23917	00	k—788
22	21993	$\frac{1}{2}s$	f—1012	59	23941	0s	e—1003
23	22015	00	g—1024	60	23961	0	{ e—1023 k—744
24	22037	0	g—1002	61	24002	6	k—702
25	22108	0	e—830	62	24090	3	k—615
26	22118	00	e—790	63	24127	0	o—3166
27	22198	0	e—710	64	24193	0	p—3160
28	22236	5s	e—702	65	24223	6b	o—3070
29	22295	0	f—700	66	24261	0	o—3029
30	22335	3	e—615	67	42284	10b	{ k—421 p—3069
31	22518	6	e—420	68	24318	10	q—3070
32	22643	3	e—295	69	24364	$\frac{1}{2}d$	q—3024
33	22742	6b	e—196	70	24387	$\frac{1}{2}$	q—3001
34	23121	5	k—1584	71	24407	2	k—298
35	23132	4	e—194	72	22435	$\frac{1}{2}$	k—270?
36	23239	$\frac{1}{2}$	e—301				
37	23265	0	k—1440				

196 (6b), (270) ($\frac{1}{2}$), 295 (2), 420 (6), 615 (3), 702 (6), 742 (0), 790 (0), 830 (0), (925) (0), 989 (0s), 1003 (10s), 1013 (00), 1024 (7), 1084 (5), 1121 ($\frac{1}{2}$), 1158 ($\frac{1}{2}$), 1176 ($\frac{1}{2}$), (1295) (0), 1321 (0), 1372 (0), 1443 (0), 1565 (0), 1584 (4), 3008 (5), 3028 (0), 3068 (10b), 3140 (0), 3165 (1).

TABLE V
Raman Spectrum of Pyridine

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	19884	$1\frac{1}{2}$	$e-3054$	32	22561	00	$e-377?$
2	21345	$\frac{1}{2}$	$e-1593$	33	23111	1	$k-1594$
3	21359	2	$e-1579$	34	23125	2	$k-1580$
4	21367	2	$e-1571$	35	23136	2	$k-1569$
5	21416*	00	$i-1579$	36	23220	1	$k-1485$
6	21461	1	$e-3055$	37	23303	0	$i-1213$
7	21494	0	$k-1444?$	38	23488*	5	$\begin{cases} i-1028 \\ k-1217 \end{cases}$
8	21533	$\frac{1}{2}$	$k-3172$	39	23525	1s	$i-991$
9	21563	$1\frac{1}{2}$	$k-3142$	40	23560	0d	$k-1145$
10	21615	$\frac{1}{2}$	$k-3090$	41	23591	0d	$e-653$
11	21642	$\frac{1}{2}$	$k-3063$	42	23647	0	$k-1058$
12	21652	8b	$k-3053$	43	23667	0	$k-1038$
13	21671	$\frac{1}{2}$	$k-3034$	44	23677	10s	$k-1028$
14	21680	$\frac{1}{2}$	$k-3025$	45	23716	10s	$k-989$
15	21719	3	$\begin{cases} e-1219 \\ k-2986 \end{cases}$	46	23726	0	$k-979$
16	21754	1	$k-2951$	47	23763	0	$k-942$
17	21797*	$\frac{1}{2}d$	$\begin{cases} e-1141 \\ k-2908 \end{cases}$	48	23827	$\frac{1}{2}$	$k-878$
18	21834	0d	$k-2871$	49	23871	00	$i-645$
19	21882	0	$e-1056$	50	23906	0	$k-799$
20	21897	0	$e-1011$	51	23930	0	$e-992$
21	21909	10s	$e-1029$	52	23968	00	$e-1030$
22	21948	10s	$e-990$	53	24052	3	$k-653$
23	21959	0	$e-979$	54	24103	$\frac{1}{2}$	$k-602$
24	21966	0	$f-1029$	55	24158*	0	$o-3073$
25	22006	$\frac{1}{2}$	$f-989$	56	24238	5b	$o-3055$
26	22047*	$\frac{1}{2}$	$\begin{cases} e-891 \\ g-992 \\ k-2658 \end{cases}$	57	24265*	0	$o-3028$
27	22256	0	$k-2449$	58	24285	0	$p-3068$
28	22286	3	$e-652$	59	24298	6b	$\begin{cases} k-407 \\ p-3055 \end{cases}$
29	22335	1	$\begin{cases} e-603 \\ k-2370 \end{cases}$	60	24318	0	$q-3070$
30	22385	0	$e-553?$	61	24335	6b	$q-3053$
31	22536	1	$e-402$	62	24356	0	$q-3032$
				63	24367	0	$q-3021$
				64	24399	1	$p-2951$
				65	24436	$1\frac{1}{2}$	$q-2952$

(377) (0), 402 (1), (553) (0), 602 (1), 652 (3), 799 (0), 878 ($\frac{1}{2}$), 942 (0), 979 (0), 990 (10), 1028 (10), 1040 (0), 1057 (0), 1143 ($\frac{1}{2}$), 1218 (3), (1444) (0), 1485 (1), 1570 (2), 1579 (2), 1594 (1), 2370 (0), 2449 (0), (2658) (0), 2871 (0), 2908 (0), 2951 (1), 2986 (0), 3025 ($\frac{1}{2}$), 3034 ($\frac{1}{2}$), 3054 (8b), 3063 ($\frac{1}{2}$), 3090 ($\frac{1}{2}$), 3142 ($1\frac{1}{2}$) 3172 ($\frac{1}{2}$)

TABLE VI
Raman Spectrum of Cyclohexane.

No.	ν	Int.	Assignment	No.	ν	Int.	Assignment
1	20001	5	$e-2937$	32	22335	0	$e-603$
2	20016	5	$e-2922$	33	22352	0	$k-2353$
3	20046	1b	$e-2892$	34	22512	1	$e-426$
4	20084	8	$e-2854$	35	22554	$\frac{1}{2}$	$e-384$
5	20238	0	$e-2700$	36	22654	$\frac{1}{2}d$	$m-2938$
6	20278	1	$e-2660$	37	22737	$\frac{1}{2}$	$m-2855$
7	20311	$\frac{1}{2}$	$e-2627$	38	22765	0	$e-173?$
8	20580	0	$e-2358$	39	22795	0	$e-143?$
9	21193	5b	$e-1445$	40	23072	0b	$i-1444$
10	21555	0d	$f-1140$	41	23265	5b	$k-1440$
11	21578	4	$i-2938$	42	23319	0d	$e-381$
12	21591	4	$\left\{ \begin{array}{l} e-1347 \\ i-2925 \end{array} \right.$	43	23357	1	$\left\{ \begin{array}{l} e-119 \\ k-1348 \end{array} \right.$
13	21662	6	$i-2854$	44	23440	5	$k-1265$
14	21672	6	$e-1266$	45	23487	1	$i-1029$
15	21768	8	$k-2937$	46	23549	3s	$k-1156$
16	21784	8	$\left\{ \begin{array}{l} e-1154 \\ k-2921 \end{array} \right.$	47	23676	5	$k-1029$
17	21807	2	$k-2928$	48	23714	4s	$i-802$
18	21817	2	$k-2888$	49	24738	1s	$e-800$
19	21835	1	$k-2870$	50	24902	10s	$k-803$
20	21852	10	$k-2853$	51	24107	0b	$k-598?$
21	21909	6	$e-1029$	52	24218	$\frac{1}{2}d$	$e-1280$
22	21946	0	$e-992$	53	24278	1	$k-427$
23	21962	0	$f-1033$	54	24352	8	$o-2941$
24	22009	1	$k-2696$	55	24369	8	$o-2924$
25	22014	00	$g-1025$	56	24426	8	$p-2927$
26	22040	2	$k-2665$	57	24440	7	$o-2853$
27	22071	1s	$k-2634$	58	24457	8	$q-2931$
28	22100	0d	$k-2605$	59	24468	8	$q-2920$
29	22136	10s	$e-802$	60	24502	8	$p-2851$
30	22192	1s	$f-803$	61	24537	10b	$q-2851$
31	22238	4b	$\left\{ \begin{array}{l} g-801 \\ k-2467? \end{array} \right.$	62	24591	1d	$o-2702$
				63	24632	2	$o-2661$
				64	24656	2	$p-2697$

384 (4), 426 (1), (600) (0), 802 (10), 1029 (6), 1156 (3), 1265 (5), 1348 (1), 1442 (5b), 2353 (0), 2467 (0), 2605 (0), 2630 (1), 2662 (2), 2698 (1), 2853 (10b), 2870 (1), 2888 (2), 2898 (2), 2922 (8), 2937 (8)

TABLE VII

Benzene

Author	Krishnamurti	Grassmann and Weiler	Infrared Absorption maxima
100 (1 <i>d</i>)	407 ($\frac{1}{2}$)	104 (1 <i>d</i>)	
606 (5)	603 (3)	606.8 (8)	
688 ($\frac{1}{2}$)	687 (0)	692 (1)	694
778 (0)		781 (1)	782
801 (0)	806 (0)	802 (0)	803
		824 ($\frac{1}{2}$)	820
850 (2)	848 (2)	849 (1 <i>d</i>)	847
979 ($\frac{1}{2}$)	976 (0)	979 (1)	971
984 (1)		981 (2)	
992.5 (10)	992 (10)	992.5 (15 <i>s</i>)	
998 (1)		(999)	
1006 ($\frac{1}{2}$)		1005 (1)	
1035 (0)	1029 (0)	1034 (1)	1025
1175 (2)	1178 (5)	1176 (1 <i>d</i>)	1183
		1285 (0)	
		1326 ($\frac{1}{2}$)	1316
1400 ($\frac{1}{2}$)	1407 (0)	1403 (2)	1379
1445 (0)		1449 (0 <i>d</i>)	
1480 (0)	1477 (0)	1480 (0)	1481
1584 (3)	1584 (3)	1585.4 (12)	1587
1605 (2)	1603 (2)	1606.4 (8)	1613
		1697 (0)	
		1827 ($\frac{1}{2}$)	1818
		1936 (1 <i>d</i>)	
		1988 ($\frac{1}{2}$)	1968
		2030 ($\frac{1}{2}$)	2040
		2128 ($\frac{1}{2}$ <i>d</i>)	
2272 (0)		2296 (1)	2260
		2358 ($\frac{1}{2}$ <i>dd</i>)	2326
2457 ($\frac{1}{2}$)	2455 ($\frac{1}{2}$)	2455 (1)	
2547 ($\frac{1}{2}$)	2543 ($\frac{1}{2}$)	2545 (1)	
2617 ($\frac{1}{2}$)		2618 (2)	
		2688 ($\frac{1}{2}$)	2667
			2856
			2894
2928 (0 <i>d</i>)	2928 (0)	2927 (1)	
2949 (5)	2948 (1)	2949 (1)	
3048 (4)	3046 (1)	3049 (8)	3010
3064 (8)	3063 (4)	3063.6 (12)	3074
3164 ($\frac{1}{2}$)	3164 ($\frac{1}{2}$)	3166.6 (3 <i>s</i>)	
3187 (1)	3187 (1)	3187.4 (4 <i>s</i>)	
		3467 (0)	
		3680 (0)	
(3910) (0)		(3916) (0)	

TABLE VIII

Toluene

Author	Howlett	Kohlrausch	Mesnage	Infra-red Absorption maxima
218 (6b)	216.7 (4)	217 (8b)	214.3 (F)	
334 ($\frac{1}{2}$)	335.0 (0)	348 (1)	341.0 (f)	
		405 (0)		
			461.4 (m)	
523 (5)	519.8 (5)	521 (7)	521.1 (m)	
(581) (0)				
622 (4b)	622.2 (3)	622 (4)	621.9 (m)	
730 (0)		729 (1)		725.6
788 (10)	786.7 (8)	785 (12)	785.8 (F)	769.3
813 (0b)	807.2 (0)			
812 (0b)	842.1 (0)	842 (1)		831.4
896 (0b)		892 (1)		897.1
978 (0)	968.3 (0)		977.0 (f)	943.4
993 ($\frac{1}{2}$ s)	992.2 (3)		990.9 (m)	980.4
1005 (10s)	1001.9 (10)	1002 (12)	1003.8 (F)	
1030 (8s)	1027.7 (6)	1032 (6)	1027.1 (m)	1028
				1077
1157 (2)	1156.5 (3)	1153 (3)	1155.4 (m)	
1181 (1)	1180.3 (3)	1176 (1)	1178.5 (ff)	1170
			1187.5 (ff)	1191
1212 (6s)	1210.0 (5)	1209 (8)	1210.0 (F)	1234
1282 (0)			1253.7 (f)	1299
1315 (0)				
1318 (0)				
1381 (2)	1379.5 (2)	1377 (3)	1378.2 (m)	1379
1402 (0)				
1434 (0)		1444 (1b)	1445.2 (f)	
1455 (0)				1457
1499 (0)				1492
1588 (2)	1585.5 (2)	1580 (1)	1585.1 (m)	1550
1606 (3)	1604.7 (3)	1603 (5b)	1604.5 (F)	1613
1630 (0)	1628.5 (00)			
				1724
				1814
				1869
				1961
				2500
			2574.5 (ff)	
			2583.3 (ff)	
			2602.4 (ff)	
			2610.7 (ff)	
		.		
		2731 ($\frac{1}{2}$)		
2868 (3vb)	2865.8 (0)	2867 (3b)	2855.5 (f)	
			2874.6 (f)	

TABLE VIII—(Contd)

Author	Howlett	Kohlrausch	Mesnage	Infra-red Absorption maxima
2922 (6 <i>b</i>)	2919.9 (4)	2917 (10 <i>b</i>)	2920.0 (<i>F</i>) 2978.9 (<i>f</i>) 3000.3 (<i>f</i>)	2994
3002 ($\frac{1}{2}$)	3004.4 (0)	3026 (4 <i>b</i>) 3055 (10 <i>rb</i>)	3056.6 (<i>m</i>) 3059.0 (0)	
3037 (4 <i>b</i>)	3035.4 (3)			
3058 (8)	3052.1 (5)			
3070 (6 <i>b</i>)	3062.5 (4) 3205.9 (0)			
				1150 4586 5848

TABLE IX *Phenol*

Author	Kohlrausch and Pongratz
243 (5 <i>b</i>)	238 (7 <i>b</i>)
507 ($\frac{1}{2}$)	504 ($\frac{1}{2}$)
532 (4)	530 (6)
590 (0)	
620 (4)	616 (5)
655 (00 <i>d</i>)	
756 (3)	751 (3)
787 (0 <i>b</i>)	
812 (8)	810 (10 <i>b</i>)
830 (3)	826 (3) 882 (00)
991 (00)	
1001 (10)	998 (12)
1013 (0)	
1027 (8 <i>s</i>)	1025 (7)
1072 (1)	1068 (0)
(1113) (0)	
1155 (3 <i>s</i>) }	1162 (5 <i>b</i>)
1170 (4 <i>s</i>) }	
1253 (2 <i>b</i>)	1253 (4 <i>b</i>)
(1425) (00)	
1464 (0)	
1498 ($\frac{1}{2}$)	
1595 (5) }	1599 (7 <i>b</i>)
1605 (5) }	
3017 ($\frac{1}{2}$ <i>b</i>)	
3051 (5) }	3060 (12 <i>b</i>)
3064 (8) }	
3085 ($\frac{1}{2}$) }	
(3150) (00 <i>d</i>)	
3200 (0 <i>b</i> <i>d</i>)	
3524 (0 <i>vb</i>)	3518 (0 <i>vb</i>)

TABLE X
Chlorobenzene.

Author	Murray and Andrews	Infra red Absorption maxima
196 (6 <i>b</i>)	198 (7)	
(270) ($\frac{1}{2}$)	275 (0)	
295 (2)	299 (2)	
420 (6)	419 (6)	
	465 (1)	
615 (3)	611 (3)	
702 (6)	703 (5)	
742 (0)	743 (1)	756
790 (0)		
830 (0)	832 (2)	820
		900
(925) (0)		
		943
989 (0 <i>s</i>)		
1003 (10 <i>s</i>)	1001 (10)	
1013 (00)		1014
1024 (7)	1023 (7)	
1084 (5)	1081 (5)	1071
1121 ($\frac{1}{2}$)	1122 (2)	1111
1158 ($\frac{1}{2}$)	1159 (3)	1149
1176 ($\frac{1}{2}$)	1171 (2)	
(1295)(0)		1250
1321 (0)	1321 (0)	1333
1372 (0)	1366 (0)	
	1102 (0)	
1443 (0)	1138 (1)	1441
	1175 (1)	1477
1565 (0)	1561 (1)	
1584 (4)	1584 (6)	1595
	2329 (0)	2326
3008 (0)	3005 (0)	
3028 (0)	3027 (0)	
3068 (10 <i>b</i>)	3069 (10)	3068
3140 (0)	3141 (0)	
3165 (1)	3166 (0)	

TABLE XI. *Pyridine*

Author	Krishnamurti	Kohlrausch and Pongratz	Infra-red Absorption maxima
(377) (0)	371 (0)		
402 (1)	403.6 (1)	401 (3)	
(553) (0)	553 (0)		
602 (1)	603 (1½)	604 (1)	
652 (3)	651.9 (3)	652 (6)	
	717 (0)		
	747 (0)		752
799 (0)	806 (0)		806.5
			810.5
			855
878 (½)	885 (1)	880 (3)	888.6
			922
942 (0)	942 (0)		950
979 (0)			
990 (10)	992 (10)	990 (15)	992.6
1028 (10)	1029.4 (10)	1028 (12)	1028
1040 (0)			
1057 (0)	1067 (1)	1066 (0)	1069
1143 (½)	1145 (1)	1144 (2)	1139
1218 (3)	1218 (3)	1207 (7)	1211
			1290
			1370
(1444) (0)	1439 (0)		1439
1485 (1)	1483 (1½)	1479 (½)	1481
1570 (2)	1571.4 (1)		
1579 (2)	1580.8 (2)	1575 (6b)	
1594 (1)	1596.7 (1)		1600
			1724
			1923
2370 (0)	2368 (½)		
2449 (0)	2455 (½)		
(2658) (0)	2651 (0)		
2871 (0)	2867 (½)		
2908 (0)	2913 (½)		
2951 (1)	2952.2 (1)	2952 (1)	
2986 (0)	2985 (½)		
3025 (½)	3024 (1)		
3034 (½)			
3054 (8b)	3054 (10)	3053 (10b)	3077
3063 (½)			
3090 (½)	3089 (½)		
3142 (1½)	3144.1 (1½)		
3172 (½)	3175 (½)		
			3390
			5848
			5883

TABLE XII.
Cyclohexane

Author	Krishnamurti	Infra-red Absorption maxima
384 ($\frac{1}{2}$)	381 ($\frac{1}{2}$)	
426 (1)	425 (1)	
(600) (0)		
	695 (0)	
802 (10)	802 (10)	840
(992) (0)	(992) (0)	909
1029 (6)	1028 (8)	1042
1156 (3)	1156 (1)	
1265 (5)	1266 (5)	1220
1318 (1)	1314 ($\frac{1}{2}$)	1323
1442 (5b)	1444 (5)	1435
2353 (0)	2351 (0)	
2467 (0)	2462 (0)	
2605 (0)		
2630 (1)	2630 (0)	
2662 (2)	2662 (1)	
2698 (1)	2695 ($\frac{1}{2}$)	
2853 (10b)	2852 (8)	2860
2870 (1)		
2888 (2)	2889 (1)	
2898 (2)		
2922 (8)	2922 (8)	
2937 (8)	2938 (8)	2940

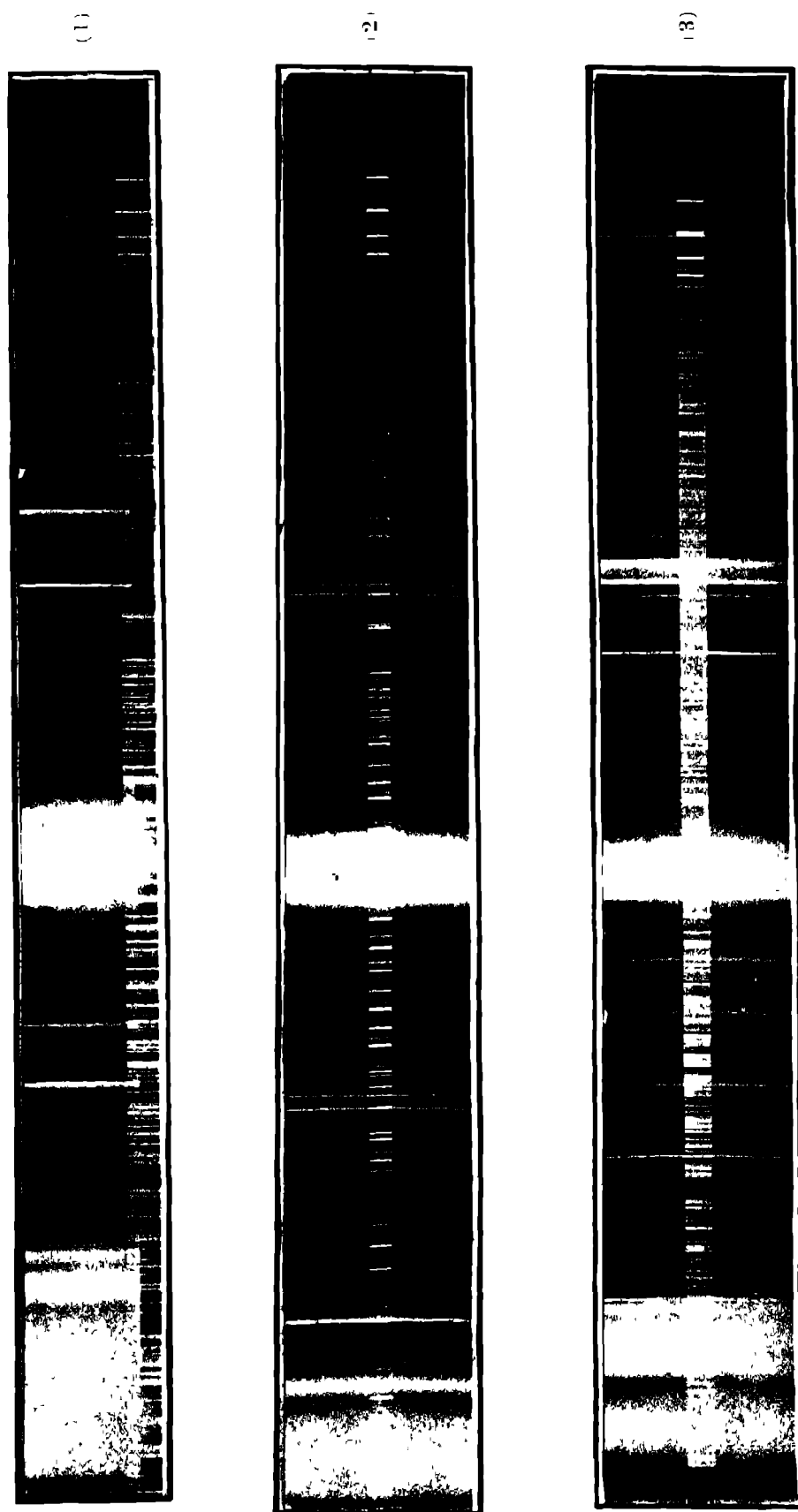


FIG. 1. Raman Spectra.

(1) Benzene, (2) Pyridine; (3) Cyclohexane.



FIG. 2. Raman Spectra

(4) Toluene, (5) Phenol, (6) Chlorobenzene.

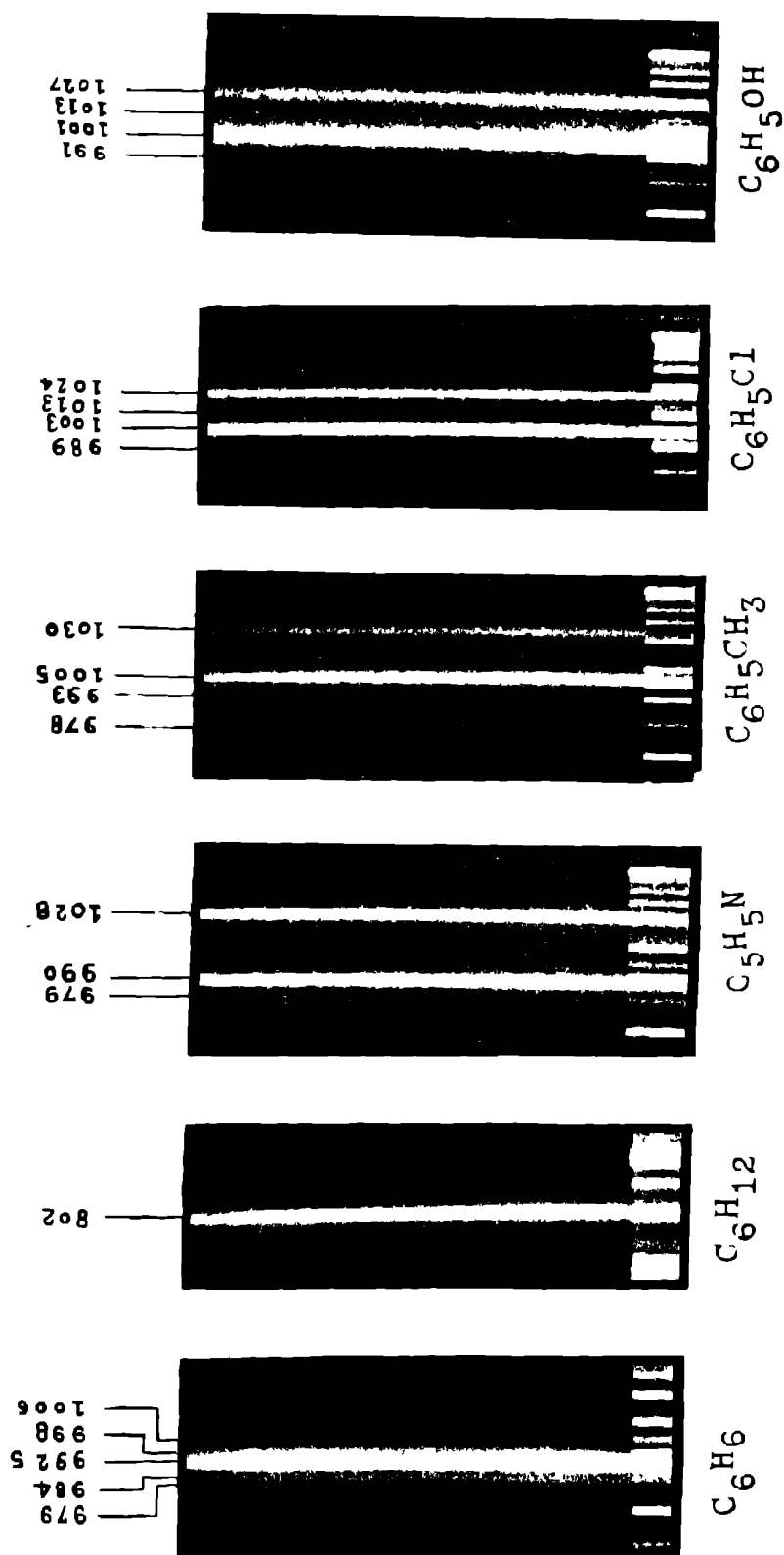


FIG. 5. Fine Structure of Raman Lines.

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES : PART III.

Doppler Effect and Coherence Phenomena.

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1 Introduction.

IN Part I¹ of this series of papers, a theory of the diffraction of light by high frequency sound waves was developed starting from the simple basic idea that the incident plane waves of light, after transmission through the medium traversed by the sound waves assume a corrugated form, owing to the fluctuations in the density and consequently also in the refractive index of the medium. The Fourier analysis of the emerging corrugated wave-front automatically gives the diffraction effects observed when the emergent waves are brought to focus by the lens of the observing telescope. The results deduced from the theory gave a gratifyingly satisfactory explanation of the observations of Bar² regarding the changes in the diffraction pattern when the supersonic intensity, the wave-length of the incident light and the length of the cell are varied.

In Part II², we extended the theory to the case of the oblique incidence of the light on the sound waves and were successful in explaining the variations of the diffraction effects reported by Debye and Sears⁴ as the angle of obliquity is varied.

In Parts I and II, we deliberately ignored the variation of the refractive index with time in order to bring out the essential features of the theory without unnecessary complications. In this the third part of the paper, we proceed to take this factor also into consideration. It will be shown that light diffracted by progressive sound waves exhibits Doppler shifts of a very simple type. In the case, however, of the diffraction of light by *standing sound waves* in a medium, we get the much more interesting result that *in any even order, radiations with frequencies $\nu \pm 2\nu^*$ would be present where ν is the frequency of the incident light, ν^* is the frequency of sound in the*

medium and r is any integer and that in an odd order, radiations with frequencies $\nu \pm \sqrt{2r+1} \nu^*$ would be present. This implies that any pair of even orders or odd orders can partly cohere and that an even order and an odd one are incoherent. This latter result has already been arrived at by Bar⁵ purely by his experimental investigations. The remarkable results of Bar in the field of supersonic research thus find a natural explanation in terms of our theory.

It should be, however, noted that the theory developed in the following is subject to the same limitations as those in the previous parts, *viz.*, that the depth of the cell is not too great to permit the form of the emerging wave-front to be deduced in the simple manner indicated in Part I. A more general consideration of the problem will be presented in a later communication.

2 Doppler effects due to a progressive sound wave

Let us suppose that the progressive sound wave travels in a direction parallel to the X-axis perpendicular to two faces of a rectangular vessel containing some homogeneous and isotropic medium. We use the same notation and the axes of reference as in our earlier paper. When the sound wave travels in the medium, the density of the medium and its refractive index undergo periodic fluctuations. If the sound wave is a simple one, we could assume that the variation of the refractive index at a point in the medium is given by

$$\mu(x, t) - \mu_0 = \mu \sin 2\pi(\nu^*t - x/\lambda^*) \quad \dots \quad (1)$$

where $\mu(x, t)$ is the refractive index of the medium at a height x from the origin at time t , μ_0 is the refractive index of the medium in its undisturbed state, μ is the maximum variation of the refractive index from μ_0 and ν^* and λ^* refer to the frequency and the wave-length of the sound wave in the medium.

Let the light wave be incident along the Z-axis perpendicular to two faces of the medium and the direction of the propagation of the sound wave. If the incident light wave is given by

$$\exp [2\pi i \nu t]$$

it will be

$$\exp [2\pi i \nu \{t - L\mu(x, t)/c\}]$$

when it arrives at the other face where L is the distance between the two faces.

The amplitude of the corrugated wave at a point on a distant screen parallel to the face of the medium from which light is emerging, whose join

with the origin has its x -direction-cosine l depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} \exp [2\pi i \{lx - \mu I_s \sin 2\pi (v^*t - x/\lambda^*)\}/\lambda] dx \quad \dots (2)$$

where p is the length of the beam along the X -axis. The real and the imaginary parts of the diffraction integral (2) are

$$\int_{-p/2}^{p/2} \{\cos ulx \cos (v \sin bx - \epsilon) - \sin ulx \sin (v \sin bx - \epsilon)\} dx \quad \dots (3)$$

and

$$\int_{-p/2}^{p/2} \{\sin ulx \cos (v \sin bx - \epsilon) + \cos ulx \sin (v \sin bx - \epsilon)\} dx$$

where $u = 2\pi/\lambda$, $b = 2\pi/\lambda^*$, $v = 2\pi\mu I_s/\lambda$ and $\epsilon = 2\pi v^*t$

Putting $bx - \epsilon$ as x' we could write the integrals* (3) as

$$\frac{2}{b} \sum_0^\infty J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \cos \left(ul \frac{x' + \epsilon}{b} \right) \cos 2rx' dx' - \frac{2}{b} \sum_0^\infty J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \sin \left(ul \frac{x' + \epsilon}{b} \right) \times \sin 2r+1 x' dx'$$

and

$$\frac{2}{b} \sum_0^\infty J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \sin \left(ul \frac{x' + \epsilon}{b} \right) \cos 2rx' dx' + \frac{2}{b} \sum_0^\infty J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \cos \left(ul \frac{x' + \epsilon}{b} \right) \times \sin 2r+1 x' dx'$$

or

$$\begin{aligned} & \frac{1}{b} \sum_0^\infty J_{2r}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \left\{ \cos \left(\frac{ul}{b} + 2rx' + \frac{ul\epsilon}{b} \right) + \cos \left(\frac{ul}{b} - 2rx' + \frac{ul\epsilon}{b} \right) \right\} dx' \\ & + \frac{1}{b} \sum_0^\infty J_{2r+1}(v) \int_{-bp/2-\epsilon}^{bp/2-\epsilon} \left\{ \cos \left(\frac{ul}{b} + 2r+1 x' + \frac{ul\epsilon}{b} \right) \right. \\ & \quad \left. - \cos \left(\frac{ul}{b} - 2r+1 x' + \frac{ul\epsilon}{b} \right) \right\} dx' \quad \dots (4a) \end{aligned}$$

* The dash over the summation sign indicates that the co-efficient of the first term has to be multiplied by half.

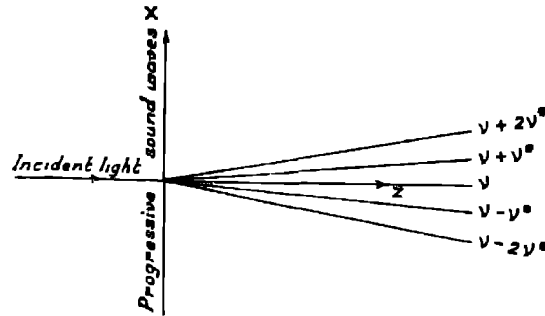


FIG. 1

The relative intensity of the m th order to the n th order is given by the expression

$$J_m^2 \left(\frac{2\pi\mu L}{\lambda} \right) / J_n^2 \left(\frac{2\pi\mu L}{\lambda} \right)$$

identical with the one given in Part I

3. Doppler effects due to a standing sound wave

In the case of a standing wave produced by the interference of two simple waves travelling in opposite directions parallel to the X-axis, we could assume that the variation of the refractive index at a point in the medium is given by

$$\mu(x, t) - \mu_0 = -\mu \sin 2\pi\nu^*t \sin (2\pi x/\lambda^*) \quad \dots \quad (8)$$

with the same notation as in the previous section. Under the same restrictions as in Part I, we find that the emerging wave-front is given by

$$\exp [2\pi i\nu \{t - L\mu(x, t)/c\}] \quad \dots \quad (9)$$

The diffraction integral is then

$$\int_{-b/2}^{b/2} \exp [2\pi i \{lx + \mu L \sin \epsilon \sin (2\pi x/\lambda^*)\}/\lambda] dx \quad \dots \quad (10)$$

where $\epsilon = 2\pi\nu^*t$.

The real and the imaginary parts of the integral (10) are

$$\int_{-b/2}^{b/2} \{\cos ulx \cos (v' \sin bx) - \sin ulx \sin (v' \sin bx)\} dx$$

and

$$\int_{-b/2}^{b/2} \{\sin ulx \cos (v' \sin bx) + \cos ulx \sin (v' \sin bx)\} dx$$

where

$$u = 2\pi/\lambda, \quad b = 2\pi/\lambda^*, \quad v' = v \sin \epsilon = (2\pi\mu L \sin \epsilon)/\lambda$$

Following the same procedure as in our earlier paper, we find that the real part of the diffraction integral (10) is

$$p \sum_0^{\infty} J_{2r} (v \sin 2\pi v^* t) \left\{ \frac{\sin [(ul + 2rb)p/2]}{(ul + 2rb)p/2} + \frac{\sin [(ul - 2rb)p/2]}{(ul - 2rb)p/2} \right\} \\ + p \sum_0^{\infty} J_{2r+1}(v \sin 2\pi v^* t) \left\{ \frac{\sin [(ul + 2r + 1)b)p/2]}{(ul + 2r + 1)b)p/2} - \frac{\sin [(ul - 2r + 1)b)p/2]}{(ul - 2r + 1)b)p/2} \right\}.$$

The integral corresponding to the imaginary part of the diffraction integral is zero.

Following similar arguments as in Part I or in the previous section we can show that the wave travelling in the direction given by

$$ul + nb = 0$$

$$\text{or} \quad \sin \theta = - \frac{n\lambda}{\lambda^*}$$

is

$$\pm J_n (v \sin 2\pi v^* t) e^{2\pi i v t} \dots \dots \dots (11)$$

multiplied by a constant usually taken out from the diffraction integral. The wave given by (11) is not a simple one but is a superposition of a number of waves given by the Fourier analysis of $J_n(v \sin 2\pi v^* t)$ and multiplied by $e^{2\pi i v t}$

Fourier Analysis of $J_n (v \sin \epsilon)$ · The well-known Neumann's addition theorem

$$J_0(\widehat{\omega}) = 2 \sum_0^{\infty} J_m(Z) J_m(z) \cos m\phi$$

where

$$\widehat{\omega} = \sqrt{Z^2 + z^2 - 2Zz \cos \phi}$$

has been generalised by Graf⁶ as

$$J_n(\widehat{\omega}) \left\{ \frac{Z - ze^{i\phi}}{Z - ze^{i\phi}} \right\}^{n/2} = \sum_{-\infty}^{+\infty} J_{n+m}(Z) J_m(z) e^{im\phi}$$

provided $|ze^{\pm i\phi}| < Z$. If n is an integer, the inequality need not be in force. Putting

$$Z = z = v/2$$

$$\text{and } \phi = 2\epsilon$$

we get

$$J_n (v \sin \epsilon) e^{-im\epsilon} (-1)^{n/2} = \sum_{-\infty}^{+\infty} J_{n+m}(v/2) J_m(v/2) e^{im\epsilon}$$

From this, changing n to $2n$ we deduce that

$$J_{2n}(v \sin \epsilon) = (-1)^n \sum_{-\infty}^{+\infty} J_{m+2n}(v/2) J_m(v/2) e^{-i(2m+2n)\epsilon}.$$

Putting $m = -n + r$ and after a little simplification, we get

$$\begin{aligned} J_{2n}(v \sin \epsilon) &= (-1)^n J_{-n}(v/2) J_n(v/2) + 2 \sum_1^{\infty} J_{-n+r}(v/2) J_{n+r}(v/2) \cos 2r\epsilon \\ &= (-1)^n 2 \sum_0^{\infty} J_{-n+r}(v/2) J_{n+r}(v/2) \cos 2r\epsilon \\ &= 2 \sum_0^{\infty} (-1)^r J_{n-r}(v/2) J_{n+r}(v/2) \cos 2r\epsilon \end{aligned}$$

Similarly we can deduce that

$$\begin{aligned} J_{2n+1}(v \sin \epsilon) &= 2 \sum_0^{\infty} (-1)^r J_{n-r}(v/2) J_{n+r+1}(v/2) \sin 2r+1\epsilon \\ J_{2n}(v \cos \epsilon) &= 2 \sum_0^{\infty} J_{n-r}(v/2) J_{n+r}(v/2) \cos 2r\epsilon \\ J_{2n+1}(v \cos \epsilon) &= 2 \sum_0^{\infty} J_{n-r}(v/2) J_{n+r+1}(v/2) \cos 2r+1\epsilon \end{aligned}$$

Returning now to the Fourier analysis of the diffraction components, the diffracted waves can be resolved into a number of simple waves, for

$$\begin{aligned} J_{2n}(v \sin 2\pi\nu^*t) e^{2\pi i\nu t} \\ &= e^{2\pi i\nu t} 2 \sum_0^{\infty} (-1)^r J_{n-r}(v/2) J_{n+r}(v/2) \cos (2r - 2\pi\nu^*t) \\ &= \sum_0^{\infty} (-1)^r J_{n-r}(v/2) J_{n+r}(v/2) \{e^{2\pi i(\nu + 2r\nu^*)t} + e^{2\pi i(\nu - 2r\nu^*)t}\} \end{aligned}$$

and

$$\begin{aligned} J_{2n+1}(v \sin 2\pi\nu^*t) e^{2\pi i\nu t} \\ &= \frac{1}{i} \sum_0^{\infty} (-1)^r J_{n-r}(v/2) J_{n+r+1}(v/2) \{e^{2\pi i(\nu + 2r+1\nu^*)t} - e^{2\pi i(\nu - 2r+1\nu^*)t}\} \end{aligned}$$

Thus in all even orders radiation frequencies

$$\nu \pm 2r\nu^*, \quad r \text{ a positive integer,}$$

are present. The relative intensity of the $\nu \pm 2r\nu^*$ sub-component in the $2n$ th order is given by

$$J_{n-r}^2(v/2) J_{n+r}^2(v/2)$$

In all odd orders radiation frequencies

$$\nu \pm 2r+1\nu^*, \quad r \text{ a positive integer,}$$

are present. (See Fig. 2.) The relative intensity of the $\nu \pm 2r+1\nu^*$ sub-component in $2n+1$ th order is given by

$$J_{n-r}^2(v/2) J_{n+r+1}^2(v/2)$$

We can conclude from the above analysis that *an even order and an odd one are incoherent while any two even or any two odd orders can partly cohere*. Any two orders symmetrically situated to the 0th order are completely coherent

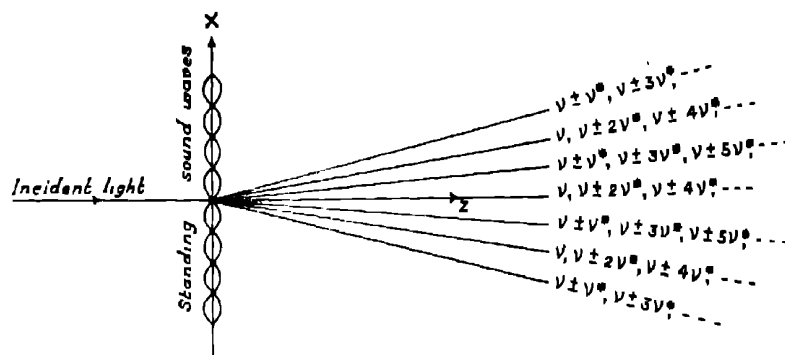


FIG. 2.

We have calculated the relative intensities of the various Doppler sub-components of the various orders as ν ranges from 0 to 5 in steps of unity and represented them in Fig 3.

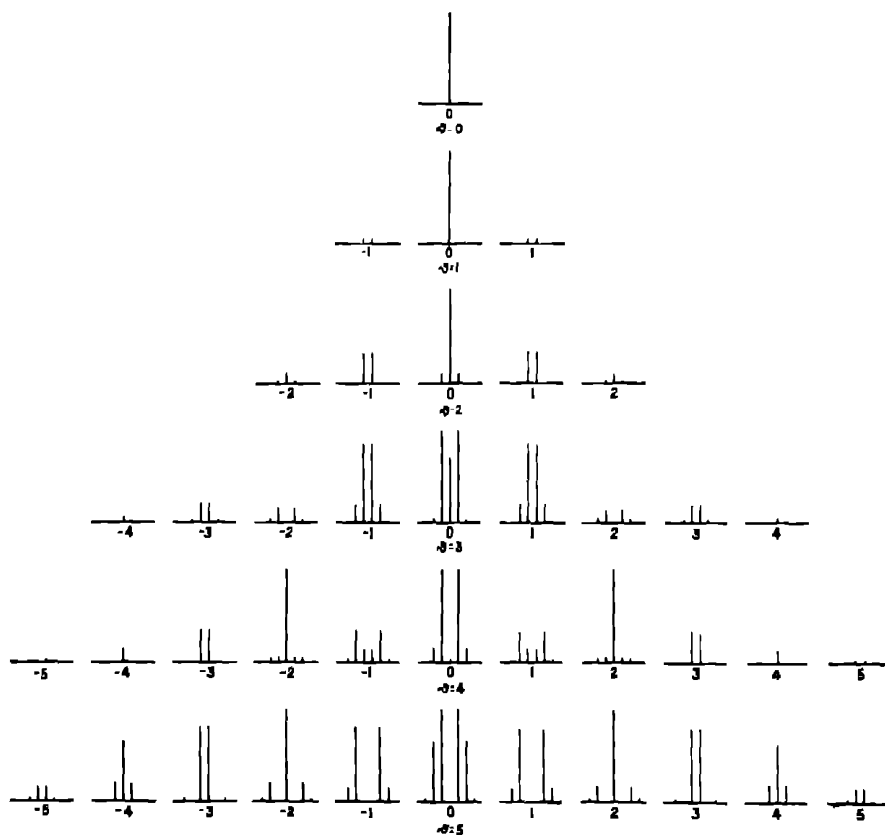


FIG. 3.

Relative intensities of the various sub-components of observable orders, the sub-components of an odd order standing on a base correspond to ---, $\nu - 2r + 1 \nu^*$, ---, $\nu - \nu^*$, $\nu + \nu^*$, ---, $\nu + 2r + 1 \nu^*$, --- and those of an even order standing on a base correspond to ---, $\nu - 2r \nu^*$, ---, ν , ---, $\nu + 2r \nu^*$, ---. In the figure $\nu = 5$, some lower orders are missing as their relative intensities are negligibly small.

We may also note that the intensity of each of the sub-components of each order depends on the amplitude of the supersonic vibration, the length of the cell and the wave-length of the incident light

If we ignore the spectral character of each order, then the relative intensity of the m th order to the n th order is

$$\frac{\int_0^{2\pi} J_m^2(v \sin \theta) d\theta}{\int_0^{2\pi} J_n^2(v \sin \theta) d\theta} \quad \text{where } v = \frac{2\pi\mu L}{\lambda}$$

which follows from Parseval's Theorem.

4 Interpretation of Bar's experimental results

Bar⁵ has recently investigated by an interference method the coherence of the diffraction components of light produced by a standing supersonic wave. He has found that the various orders could be classed into two groups, one comprising the even orders and the other comprising the odd orders and that any two orders of a group cohere partly while two orders from different groups are completely incoherent. These results are readily understood when we notice that an even order contains radiations with frequencies $\nu \pm 2r\nu^*$ while an odd order contains radiations with frequencies $\nu \pm (2r+1)\nu^*$. The experimental results of Bar are thus fully explicable in terms of the theory we have developed in the previous section. Bar has himself remarked that the observed coherence indicates the presence of a series of frequency components in each of the diffraction spectra. It will be noticed that, according to our theory, even the zero-order spectrum includes such a series of frequency components.

5. Summary.

The theory developed in Part I of this series of papers has been developed in this paper to find the Doppler effects in the diffraction components of light produced by the passage of light through a medium containing (1) a progressive supersonic wave and (2) a standing supersonic wave.

(1) In the case of the former the theory shows that the n th order which is inclined at an angle $\sin^{-1}\left(-\frac{n\lambda}{\lambda^*}\right)$ to the direction of the propagation of the incident light has the frequency $\nu - n\nu^*$ where ν is the frequency of light, ν^* is the frequency of sound and n is a positive or negative integer and that the n th order has the relative intensity $J_n^2\left(\frac{2\pi\mu L}{\lambda}\right)$ where μ is the maximum variation of the refractive index, L is the distance between the faces of the cell of incidence and emergence and λ is the wave-length of light.

(2) In the case of a standing supersonic wave, the diffraction orders could be classed into two groups, one containing the even orders and the other odd orders; any even order, say $2n$, contains radiations with frequencies $\nu \pm 2r\nu^*$ where r is an integer including zero, the relative intensity of the $\nu \pm 2r\nu^*$ sub-component being $J_{n-r}^2 \left(\frac{\pi\mu I_0}{\lambda} \right) J_{n+r}^2 \left(\frac{\pi\mu I_0}{\lambda} \right)$; any odd order, say $2n+1$, contains radiations with frequencies $\nu \pm (2r+1)\nu^*$, the relative intensity of the $\nu \pm (2r+1)\nu^*$ sub-component being $J_{n-r}^2 \left(\frac{\pi\mu I_0}{\lambda} \right) J_{n+r+1}^2 \left(\frac{\pi\mu I_0}{\lambda} \right)$. These results satisfactorily interpret the recent results of Bar that any two odd orders or even ones partly cohere while an odd one and an even one are incoherent.

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UNITARY THEORY OF FIELD AND MATTER.

II. Classical Treatment. Charged Particle with Electric and Magnetic Moment.

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Introduction

IN the preceding paper we have derived Kramers's "classical" equations of motion of a spinning electron from the unitary field theory. This seems very satisfactory, but we have already mentioned in the conclusion of that paper that a closer examination of the problem leads to serious difficulties. We shall explain these here and proceed then to avoid them by more general assumptions.

1. Kramers's "classical" equations of motion of the spinning electron.

Following Kramers's reasoning, we write the equations of motion I, (5, 42), (5, 43), (5, 44) for the rest system.

$$(1, 1) \quad \begin{cases} \frac{d\vec{G}}{dt} = e\vec{E}, & \frac{dE}{dt} = 0, \\ \frac{d\vec{M}}{dt} = \vec{B} \times \vec{m}, & \frac{d\vec{P}}{dt} = \vec{E} \times \vec{m} \end{cases}$$

They hold also in any system for a slow moving particle where \vec{v} and

$$(1, 2) \quad \vec{p} = \vec{m} \times \vec{v}$$

are small quantities.

Now (\vec{m}, \vec{p}) and (\vec{M}, \vec{P}) are two 6-vectors. Kramers assumes that they are proportional, writing

$$(1, 3) \quad \vec{m} = a\vec{M}, \quad \vec{p} = a\vec{P}.$$

Now from (1, 1) it follows that

$$(1, 4) \quad E = E_0 = \mu$$

is a constant, the rest-mass, and

$$(1, 5) \quad \frac{d\vec{G}}{dt} = \mu \frac{d\vec{v}}{dt} = e \vec{E},$$

therefore

$$(1, 6) \quad \frac{d\vec{p}}{dt} = a \frac{d\vec{P}}{dt} = a (\vec{E} \times \vec{m}) = \frac{a\mu}{e} \left(\frac{d\vec{v}}{dt} \times \vec{m} \right).$$

But from (1, 2) one has, for small \vec{v} ,

$$(1, 7) \quad \frac{d\vec{p}}{dt} = \vec{m} \times \frac{d\vec{v}}{dt}$$

(1, 6) and (1, 7) are compatible only if

$$(1, 8) \quad a = -\frac{e}{\mu}.$$

Since a is the ratio of magnetic moment and angular momentum, we have derived the fundamental formula of Uhlenbeck and Goudsmit's theory of the spinning electron (usually expressed in common units as the assumption that the ratio $\frac{m}{M}$ is $\frac{e}{\mu c}$ — not $\frac{e}{2\mu c}$ as for the orbital motion).

2 Critical considerations.

From Kramers's standpoint this seems to be extremely welcome, it indicates that the main property of the spin can be described by classical mechanics.

But from the standpoint of the unitary field theory the situation is not at all satisfactory

For in this theory, one should expect the problem of determining the motion of a singularity in a constant external field must have a definite solution whatever the Lagrangian L may be (if it satisfies only the conditions of relativity invariance). But the condition (1, 8) which can be written

$$(2, 1) \quad \frac{\vec{M}_0}{\vec{P}_0} = \frac{\vec{m}}{e}$$

is a condition restricting L , for the left-hand term is the ratio of integrals depending on the solution of the field equations, *i.e.*, on L . We shall explain this for the case of quasi-stationary motion, where the acceleration of the singularity is so small that the inner field in the rest system can be considered as static:

$$(2, 2) \quad \begin{cases} \text{rot } \vec{E}^0 = 0, & \text{div } \vec{D}^0 = 0. \quad \text{Electro-static field} \\ \text{rot } \vec{H}^0 = 0, & \text{div } \vec{B}^0 = 0: \quad \text{Magneto-static field} \end{cases}$$

We have to solve these equations under the boundary conditions

$$(2, 3) \quad \left\{ \begin{array}{l} \int_0 (\vec{n} \cdot \vec{D}^0) d\sigma = e, \\ \int_0 (\vec{a} \times \vec{r}) \cdot (\vec{n} \times \vec{E}^0) d\sigma = 0 \end{array} \right\} \text{electric boundary conditions,}$$

$$(2, 4) \quad \left\{ \begin{array}{l} \int_0 (\vec{n} \cdot \vec{B}^0) d\sigma = 0, \\ \int_0 (\vec{a} \times \vec{r}) \cdot (\vec{n} \times \vec{H}^0) d\sigma = \vec{a} \times \vec{m} \end{array} \right\} \text{magnetic boundary conditions,}$$

(where \vec{a} is an arbitrary vector), and

$$(2, 5) \quad \left\{ \begin{array}{l} \int_0 (\vec{X} \cdot \vec{n}) d\sigma = 0, \dots \\ \int_0 (\vec{S} \cdot \vec{n}) d\sigma = 0, \int_0 \vec{r} \cdot (\vec{S} \times \vec{n}) d\sigma = 0 \end{array} \right\} \text{dynamical conditions.}$$

The distribution of the field depends linearly on e and \vec{m} , which can be arbitrarily given, but also essentially on the Lagrangian I_1 , which determines the functions representing D^0 , H^0 in terms of E^0 , B^0 . Therefore

$$(2, 6) \quad \vec{E}_0 = \int (I_1 + E^0 D^0) dv, \quad \vec{M}_0 = \int [\vec{r} \times (D^0 \times B^0)] dv$$

depend also on the choice of I_1 , and there seems to be no general theorem which guarantees the fulfilment of the relation (2, 1).

If Kramers's arguments are considered as right they would imply a sharp condition for the choice of the Lagrangian I_1 , the analytical meaning of which is rather obscure.

But I do not believe that Kramers's considerations are convincing, since the spin $\frac{1}{2}$ of the electron has no classical analogy. It is well known that the spin is closely connected with the two valued representation of the Lorentz-group which cannot be interpreted in terms of classical theory. The classical analogy of a particle with the spin $\frac{1}{2}$ is the non-rotating system; the value $\frac{1}{2}$ means a kind of zero-point rotation—just as the zero-point energy of the linear oscillator $\frac{1}{2} h\nu$ corresponds classically to the non-oscillating state.

My collaborator Pryce has recently put forward the idea that the state of one-quantum rotation represents the proton, and I have confirmed this

by an estimate of the mass-ratio, proton : electron ¹. If this idea is sound Kramers's considerations leading to (2, 1) should not be considered as stringent. Then the problem arises how to modify the theory to avoid these conclusions.

It is clear that they spring from the assumption of a pure magnetic moment in the rest-system, expressed by (1, 2). This assumption leads also to other difficulties, if one combines it with the simplest Lagrangian which in the rest-system has the expression

$$(2, 7) \quad L = \sqrt{1 + B_0^2 - E_0^2} - 1$$

For there exists no statical solution for an uncharged particle with a magnetic moment. In this case one has

$$(2, 8) \quad \vec{B}_0 = \frac{\vec{H}_0}{\sqrt{1 - H_0^2}},$$

and \vec{H}_0 has a singularity of the character of a classical dipole. Then (2, 8) shows that B_0 becomes infinite at a finite distance from the singularity of \vec{H}_0 .²

This difficulty may disappear if besides the magnetic moment the particle has a charge, or an electric moment or both. We shall therefore modify the theory given in Part I so as to represent the motion of a charged particle having in the rest-system an electric and a magnetic moment \vec{p}_0 and \vec{m}_0 . We do this chiefly because the generalised theory, owing to its higher symmetry, is mathematically more perfect. The question whether such a system is likely to represent a real particle will be touched at the end of this communication.

3. Charged particle with electric and magnetic moment.

We use the notations of Part I with a few modifications which shall be given here.

The orbit of the singularity is given by the vector $\vec{r}_0(t)$, its velocity by $\vec{v}(t) = \frac{d\vec{r}_0}{dt}$. We introduce the 4-vector

$$(3, 1) \quad (v^1, v^2, v^3, v^4) = \left(\frac{v}{a}, \frac{1}{a} \right), \quad a = \sqrt{1 - v^2}.$$

¹ M. Born, *Nature*, 1935, 136, 952.

² The reason for the difference of the electrostatic and magnetostatic cases is the difference of the signs of B_0^2 and E_0^2 in (2, 7). In the electric case the corresponding formula to (2, 8) is $\vec{E}_0 = \vec{D}_0 / \sqrt{1 + D_0^2}$; there \vec{D}_0 has an infinity, but \vec{E}_0 remains finite.

$\delta_0(\vec{r} - \vec{r}_0)$ is a 3-dimensional δ -function in the rest-system, and

$$(3, 2) \quad \delta(\vec{r} - \vec{r}_0, t) = \frac{\delta_0}{\sqrt{1 - v^2}} = \frac{\delta_0}{\alpha}$$

the corresponding δ -function in any system. One has

$$(3, 3) \quad \int f \delta_0 dv_0 = \int f \delta dv = f(\vec{r}_0)$$

The electric rest-density is

$$(3, 4) \quad \rho_0 = e \delta_0$$

where e is the electric charge

The 4-vector current-density is given by

$$(3, 5) \quad (\rho^1, \rho^2, \rho^3, \rho^4) = \rho_0(v^1, v^2, v^3, v^4) = \left(\frac{\rho_0}{\alpha} \vec{v}, \frac{\rho_0}{\alpha} \right),$$

or, if we introduce the density

$$(3, 6) \quad \rho = \frac{\rho_0}{\alpha} = \frac{e \delta_0}{\alpha} = e \delta,$$

we have

$$(3, 7) \quad (\rho^1, \rho^2, \rho^3, \rho^4) = (\rho \vec{v}, \rho) = (e \vec{v} \delta, e \delta)$$

The continuity equation is

$$(3, 8) \quad \frac{\partial e v^k \delta}{\partial x^k} = 0, \quad \text{or} \quad e \vec{v} \text{ grad } \delta + \frac{\partial e \delta}{\partial t} = 0.$$

Integrating this over space, one gets

$$(3, 9) \quad \frac{de}{dt} = 0, \quad e = \text{const.}$$

Multiplying (3, 8) by x and then integrating, one has

$$\int x \left(v_x \frac{\partial \delta}{\partial x} + v_y \frac{\partial \delta}{\partial y} + v_z \frac{\partial \delta}{\partial z} \right) dv + \frac{d}{dt} \int x \delta dv = 0,$$

or

$$-v_x + \frac{dx_0}{dt} = 0, \dots\dots$$

in agreement with the definition of \vec{v} .

The electric moment is assumed to be a space vector in the rest-system, \vec{p}_0 ; it corresponds to a 4-vector

$$(3, 10) \quad (p^1, p^2, p^3, p^4) = [\vec{p}_0, (\vec{v} \vec{p}_0)],$$

satisfying the condition

$$(3, 11) \quad v^k p_k = 0.$$

In the same way one has for the magnetic moment

$$(3, 12) \quad (m^1, m^2, m^3, m^4) = [\vec{m}_0, (\vec{v} \times \vec{m}_0)],$$

$$(3, 13) \quad v^k m_k = 0.$$

The corresponding part of the Lagrangian must be a simultaneous invariant of the three 4-vectors v^k , p^k , m^k and the field 6-vector f_{kl} which reduces to

$$\vec{m}_0 \vec{B} - \vec{p}_0 \vec{E}$$

in the rest-system. To construct this invariant, we form first the 6-vector³

$$(3, 14) \quad m^{kl} = (v^k p^l - v^l p^k) + (v^k m^l - v^l m^k)^*$$

and write

$$(3, 15) \quad (m_{23}, m_{31}, m_{12}) = \frac{1}{a} \vec{m}, \quad (m_{14}, m_{24}, m_{34}) = \frac{1}{a} \vec{p},$$

where

$$(3, 16) \quad \begin{cases} \vec{p} = \vec{p}_0 - \vec{v} (\vec{p}_0 \cdot \vec{v}) - (\vec{v} \times \vec{m}_0), \\ \vec{m} = \vec{m}_0 - \vec{v} (\vec{m}_0 \cdot \vec{v}) + (\vec{v} \times \vec{p}_0). \end{cases}$$

Then the invariant in question is evidently

$$(3, 17) \quad \frac{1}{2} m^{kl} f_{kl} = \frac{1}{2} \{ (v^k p^l - v^l p^k) + (v^k m^l - v^l m^k)^* \} f_{kl} = \vec{m} \vec{B} - \vec{p} \vec{E}.$$

Since for any two tensors f_{kl} , g_{kl} there is $f_{kl} g^{*kl} = f^{*kl} g_{kl}$ we write (3, 17) as

$$(3, 18) \quad \frac{1}{2} m^{kl} f_{kl} = f_{kl} v^k p^l + f^{*kl} v^k m^l = (f_{kl} p^l + f^{*kl} m^l) v^k.$$

The first of these expressions may be interpreted as the negative work done by the electric and magnetic forces:

$$(3, 19) \quad \begin{cases} f_{kl} v^l = \frac{1}{a} [\vec{E} + (\vec{v} \times \vec{B})], \\ f^{*kl} v^l = \frac{1}{a} [\vec{B} - (\vec{v} \times \vec{E})] \end{cases}$$

on the electric and magnetic rest-momenta \vec{p}_0 , \vec{m}_0 .

The Lagrangian of the singularity is

$$(3, 20) \quad \begin{cases} l\delta = \delta_0 (e v^k \phi_k + \frac{1}{2} m^{kl} f_{kl}) \\ = \delta (e\phi - e \vec{v} \cdot \vec{A} + \vec{m} \cdot \vec{B} - \vec{p} \cdot \vec{E}) \end{cases}$$

in complete agreement with I, (3, 1)

³ a^{*kl} is the dual tensor of a_{kl} , one has $a^{*23} = a_{14}$, ..., $a^{*14} = a_{23}$, ..., but $a^{*13} = -a^{14}$, ..., $a^{*14} = -a^{23}$, ...; or $a^{*23} = -a^{14}$, ..., $a^{*14} = a^{23}$, ..., and $a^{*23} = a_{14}$, ..., $a^{*14} = -a_{23}$, ...

4. Field equations and boundary conditions.

The field equations are exactly the same as those given in I, (1, 5), (1, 6). We write only the essential set

$$(4, 1) \quad \frac{\partial p^{kl}}{\partial x^l} = \rho_0 v^k - \frac{\partial m^{kl} \delta}{\partial x^l},$$

or

$$(4, 2) \quad \begin{cases} \text{rot } \vec{H} - \dot{\vec{D}} = \delta(e \vec{v} + \dot{\vec{p}}) - \text{rot } (\vec{m} \delta), \\ \text{div } \vec{D} = \delta e - \text{div } (\vec{p} \delta) \end{cases}$$

As explained in I, one can replace the right-hand terms by 0, adding the boundary conditions

$$(4, 3) \quad \begin{cases} \int_0 (\vec{n} \times \vec{H}) d\sigma = e \vec{v} + \dot{\vec{p}}, & \int_0 \vec{n} \cdot \vec{D} d\sigma = e, \\ \int_0 (\vec{n} \times \vec{E}) d\sigma = 0, & \int_0 \vec{n} \cdot \vec{B} d\sigma = 0, \end{cases}$$

$$(4, 4) \quad \begin{cases} \int_0 (\vec{a} \cdot \vec{r}) (\vec{n} \times \vec{H}) d\sigma = \vec{a} \times \vec{m}, & \int_0 \vec{r} (\vec{n} \cdot \vec{D}) d\sigma = e \vec{r}_0 + \dot{\vec{p}}, \\ \int_0 (\vec{a} \cdot \vec{r}) (\vec{n} \times \vec{E}) d\sigma = 0, & \int_0 \vec{r} (\vec{n} \cdot \vec{B}) d\sigma = 0, \end{cases}$$

where \vec{a} is an arbitrary vector.

5. Dynamical boundary conditions.

For the variation of the world line of the singularity we use the second expression (3, 18), then we have the variation problem

$$(5, 1) \quad \int \delta_0 (e \phi_k + f_{kl} p^l + f^*_{kl} m^l) \dot{x}^k dv_0 d\tau = \text{Extremum},$$

with the conditions

$$(5, 2) \quad \dot{x}^k \dot{x}_k = 1, \quad \dot{x}^k p_k = 0, \quad \dot{x}^k m_k = 0;$$

the first of these expresses that τ is the proper time, the others are a repetition of (3, 11), (3, 13).

We vary first p^l and m^l ; with the help of two Lagrangian multipliers λ_1, λ_2 , we get

$$(5, 3) \quad \begin{cases} f_{kl} \dot{x}^k + \lambda_1 \dot{x}^l = 0, \\ f^*_{kl} \dot{x}^k + \lambda_2 \dot{x}^l = 0. \end{cases}$$

Multiplication with \dot{x}^l and summation gives

$$(5, 4) \quad \begin{cases} \lambda_1 = -f_{kl} \dot{x}^k \dot{x}^l = 0, \\ \lambda_2 = -f^*_{kl} \dot{x}^k \dot{x}^l = 0, \end{cases}$$

since f_{kl} is antisymmetric. Therefore (5, 3) reduces to

$$(5, 5) \quad f_{kl} \dot{x}^k = 0, \quad f^*_{kl} \dot{x}^k = 0,$$

or

$$(5, 6) \quad [\vec{E} + (\vec{v} \times \vec{B})]_0 = 0, \quad [\vec{B} - (\vec{v} \times \vec{E})]_0 = 0.$$

The electric and magnetic "Lorentz-force" vanishes at the singularity.⁴

Since λ_1, λ_2 vanish, the second and third condition (5, 2) can be omitted. The first condition (5, 2) corresponds to a Lagrangian multiplier μ . Varying x^n , we get

$$(5, 7) \quad \iiint \delta_0 \left\{ \frac{d\mu \dot{x}_n}{dt} - K_n \right\} dv_0 = 0,$$

or symbolically

$$(5, 8) \quad \left[\frac{d\mu \dot{x}_n}{dt} - K_n \right]_0 = 0,$$

where

$$K_n = \frac{\partial}{\partial x^n} (e\phi_k + f_{kl}p^l + f^*_{kl}m^l) \dot{x}^n - \frac{d}{d\tau} (e\phi_n + f_{nl}p^l + f^*_{nl}m^l)$$

or

$$(5, 9) \quad K_n = \left\{ ef_{kn} + \left(\frac{\partial f_{kl}}{\partial x^n} - \frac{\partial f_{kl}}{\partial x^k} \right) p^l + \left(\frac{\partial f^*_{kl}}{\partial x^n} - \frac{\partial f^*_{kl}}{\partial x^k} \right) m^l \right\} \dot{x}^k.$$

The bracket is antisymmetric in k, n ; therefore

$$(5, 10) \quad K_n x^n = 0.$$

Multiplying (5, 8) by \dot{x}^n we have

$$\dot{x}^n \frac{d\mu \dot{x}_n}{dt} = \mu \dot{x}^n \ddot{x}_n + \dot{\mu} \dot{x}^n \dot{x}_n = 0,$$

or, since $\dot{x}^n \dot{x}_n = 1$, $\dot{x}^n \ddot{x}_n = 0$.

$$(5, 11) \quad \dot{\mu} = 0, \quad \mu = \text{const.}$$

⁴ We remind the reader that the vanishing of a quantity at the singularity, written symbolically $f_0 = 0$ means really $\int_0 \delta_0 f dv_0 = 0$. For instance, for the Lagrangian

$L = \sqrt{1 - \vec{E}^2} - 1$ the field of a point charge is $\vec{E} = \frac{e}{\sqrt{e^2 + r^4}} \cdot \frac{\vec{r}}{r}$, it has a "harmless" singularity at $r = 0$, i.e., E_x jumps from -1 to $+1$ if one passes the singular point along the X-axis. But one has

$$\int_0 \delta_0 E_x dv_0 = \int_0 \delta_0 \frac{x}{r} dv_0 = 0,$$

or symbolically $(E_x)_0 = 0$. The expressions (5, 6), etc., have to be interpreted in the same way.

μ represents therefore (as in Part I) a constant rest-mass attached to the singularity. According to the fundamental idea of the unitary theory, we put

$$(5, 12) \quad \mu = 0$$

and have

$$(5, 13) \quad [K_{\mu}]_0 = 0.$$

Taking account of (5, 5), this means

$$(5, 14) \quad [K_{\mu}]_0 = \left[\left\{ \left(\frac{\partial f_{kl}}{\partial x^i} - \frac{\partial f_{il}}{\partial x^k} \right) p^l + \left(\frac{\partial f^{*kl}}{\partial x^i} - \frac{\partial f^{*il}}{\partial x^k} \right) m^l \right\} \dot{x}^k \right]_0 = 0.$$

In the rest-system the dynamical conditions (5, 6), (5, 14) reduce to

$$(5, 15) \quad \begin{cases} \vec{E}_0 = 0, \quad \vec{B}_0 = 0, \\ \vec{K}_0 = - [\text{grad} (\vec{B} \vec{m}_0 - \vec{E} \vec{p}_0)]_0 = 0. \end{cases}$$

6. Conservation Laws.

The conservation laws can be taken over unchanged from Part I, (4, 5):

$$(6, 1) \quad \frac{\partial T_k^l}{\partial x^l} = \delta_0 f_{kn} \rho^n + \frac{1}{2} f_{nl} \frac{\partial (m^{nl} \delta)}{\partial x^k} - \frac{\partial (t_k^l \delta)}{\partial x^l},$$

where

$$(6, 2) \quad t_k^l = \lambda \delta_k^l - m^{ln} f_{kn},$$

$$(6, 3) \quad \lambda = \frac{1}{2} m^{nl} f_{nl};$$

or, in space-vector notation [I, (4, 14)] for the rest-system:

$$(6, 4) \quad \begin{cases} \frac{\partial \rho_x}{\partial t} + \text{div } \vec{X} = \delta_0 e \vec{E}_x + \vec{B} \frac{\partial (\vec{m}_0 \delta_0)}{\partial x} - \vec{E} \frac{\partial (\vec{p}_0 \delta_0)}{\partial x} - \delta_0 \dot{s}_x - \text{div } (\vec{x} \delta_0), \\ \frac{\partial U}{\partial t} + \text{div } \vec{S} = \delta_0 (\vec{B} \vec{m}_0 - \vec{E} \vec{p}_0) - \delta_0 u - \text{div } (\vec{s} \delta_0). \end{cases}$$

Integrating over a small sphere surrounding \vec{r}_0 , and using (5, 15), one gets

$$(6, 5) \quad \begin{cases} \int_0 (\vec{X} \vec{n}) d\sigma = - \left[\vec{m}_0 \frac{\partial \vec{B}}{\partial x} - \vec{p}_0 \frac{\partial \vec{E}}{\partial x} \right]_0 = - [K_x]_0 = 0, \\ \int_0 (\vec{S} \vec{n}) d\sigma = \left[\vec{m}_0 \vec{B} - \vec{p}_0 \vec{E} \right]_0 = 0. \end{cases}$$

In the same way one finds

$$(6, 6) \quad \int_0 (\vec{N}_x \vec{n}) d\sigma = 0,$$

where \vec{N}_x is defined in Part I, (4, 17), and

$$(6, 7) \quad \int_0 \vec{r} (\vec{S} \vec{n}) d\sigma = 0.$$

For all fields satisfying the boundary conditions (6, 5), (6, 6), (6, 7) one has the conservative in laws

$$(6, 8) \quad \begin{cases} \frac{\partial \vec{S}_r}{\partial t} + \text{div } \vec{X} = 0, \dots \\ \frac{\partial U}{\partial t} + \text{div } \vec{S} = 0. \end{cases}$$

7. Equations of motion in a constant field.

The considerations of I, section 5, can be transferred without change to our more general case. We have [I (5, 4), (5, 5)] :

$$(7, 1) \quad \begin{cases} \frac{dG}{dt} + \int_0^\infty (\vec{X} \vec{n}) d\sigma = 0, \dots \\ \frac{dE}{dt} + \int_0^\infty (\vec{S} \vec{n}) d\sigma = 0, \end{cases}$$

$$(7, 2) \quad \begin{cases} \frac{dM_x}{dt} + \int_0^\infty (\vec{N}_x \vec{n}) d\sigma = 0, \dots \\ \frac{dE_q}{dt} - \vec{G} + \int_0^\infty \vec{r} (\vec{S} \vec{n}) d\sigma = 0 \end{cases}$$

Splitting the field into an external and an internal field we get [I (5, 11), (5, 12)] :

$$(7, 3) \quad \begin{cases} \vec{G} = \vec{G}' + (\vec{D}^e \times \int \vec{B}' dv) - (\vec{B}^e \times \int \vec{D}' dv), \\ M_x = M_x' + D_x^e \int (\vec{r} \vec{B}') dv - \vec{D}^e \cdot \int \vec{r} B_{x'} dv \\ \quad - B_x^e \int (\vec{r} \vec{D}') dv + \vec{B}^e \cdot \int \vec{r} D_{x'} dv; \end{cases}$$

and [I (5, 33), (5, 3)] :

$$(7, 4) \quad \begin{cases} \frac{dE}{dt} = \frac{dE'}{dt} + \vec{H}^e \cdot \int \dot{\vec{B}}' dv + \vec{E}^e \cdot \int \dot{\vec{D}}' dv, \\ \frac{dE_q}{dt} = \frac{dE'_q}{dt} + \vec{H}^e \cdot \int x \dot{\vec{B}}' dv + \vec{E}^e \cdot \int x \dot{\vec{D}}' dv, \\ \vec{G} = \vec{G}' + (\vec{E}^e \times \int \vec{H}' dv) - (\vec{H}^e \times \int \vec{E}' dv). \end{cases}$$

On the other hand the scalar products in the surface integrals (7, 1) have the values I, (5, 15), (5, 16), (5, 17) :

$$(7, 5) \quad \left\{ \begin{aligned} \vec{X} \cdot \vec{n} &= (\vec{X}^e \cdot \vec{n}) + H_x^e (\vec{B}^i \cdot \vec{n}) + E_x^e (\vec{D}^i \cdot \vec{n}) \\ &\quad - [\vec{B}^e \times (\vec{n} \times \vec{H}^i)]_x - [\vec{D}^e \times (\vec{n} \times \vec{E}^i)]_x \\ \vec{S} \cdot \vec{n} &= (\vec{S}^e \cdot \vec{n}) - \vec{E}^e \cdot (\vec{n} \times \vec{H}^i) + \vec{H}^e \cdot (\vec{n} \times \vec{E}^i), \\ \vec{N}_x \cdot \vec{n} &= (\vec{N}_x^e \cdot \vec{n}) + (\vec{B}^e \cdot \vec{r}) (\vec{n} \times \vec{H}^i)_x - B_x^e \vec{r} \cdot (\vec{n} \times \vec{H}^i) \\ &\quad + (\vec{D}^e \cdot \vec{r}) (\vec{n} \times \vec{E}^i)_x - D_x^e \vec{r} \cdot (\vec{n} \times \vec{E}^i) \\ &\quad - (\vec{H}^e \times \vec{r})_x (\vec{n} \cdot \vec{B}^i) - (\vec{E}^e \times \vec{r})_x (\vec{n} \cdot \vec{D}^i). \end{aligned} \right.$$

We shall now proceed (deviating from I) without specialising the co-ordinate system. Integrating the field equations (4, 2) and taking account of the boundary conditions (4, 3), (4, 4) we get

$$(7, 6) \quad \left\{ \begin{aligned} \int_{\infty}^{\infty} (\vec{n} \times \vec{H}^i) d\sigma &= \int \dot{\vec{D}}^i dv - e \vec{v} - \vec{p}, & \int_{\infty}^{\infty} \vec{n} \cdot \vec{D}^i d\sigma &= -e, \\ \int_{\infty}^{\infty} (\vec{n} \times \vec{E}^i) d\sigma &= - \int \dot{\vec{B}}^i dv, & \int_{\infty}^{\infty} \vec{n} \cdot \vec{B}^i d\sigma &= 0, \end{aligned} \right.$$

$$(7, 7) \quad \left\{ \begin{aligned} \int_{\infty}^{\infty} (\vec{a} \cdot \vec{r}) (\vec{n} \times \vec{H}^i) d\sigma &= \int \{ (\vec{a} \cdot \vec{r}) \dot{\vec{D}}^i + (\vec{a} \times \vec{H}^i) \} dv - (\vec{a} \times \vec{m}), \\ \int_{\infty}^{\infty} \vec{r} (\vec{n} \cdot \vec{D}^i) d\sigma &= \int \vec{D}^i dv - e \vec{r}_0 - \vec{p}; \end{aligned} \right.$$

$$(7, 8) \quad \left\{ \begin{aligned} \int_{\infty}^{\infty} (\vec{a} \cdot \vec{r}) (\vec{n} \times \vec{E}^i) d\sigma &= - \int \{ (\vec{a} \cdot \vec{r}) \dot{\vec{B}}^i - (\vec{a} \times \vec{E}^i) \} dv, \\ \int_{\infty}^{\infty} \vec{r} (\vec{n} \cdot \vec{B}^i) d\sigma &= \int \vec{B}^i dv \end{aligned} \right.$$

Introducing this into (7, 1), (7, 2) one finds (omitting the indices e, i) :

$$(7, 9) \quad \left\{ \begin{aligned} \frac{d\vec{G}}{dt} &= e[\vec{E} + (\vec{v} \times \vec{B})] + (\dot{\vec{p}} \times \vec{B}), \\ \frac{d\vec{F}}{dt} &= e(\vec{v} \cdot \vec{E}) + (\dot{\vec{p}} \cdot \vec{E}), \end{aligned} \right.$$

$$(7, 10) \quad \left\{ \begin{aligned} \frac{d\vec{M}}{dt} &= (\vec{B} \times \vec{m}) - (\vec{E} \times \vec{p}) - e(\vec{E} \times \vec{r}_0), \\ \frac{d\vec{E} \cdot \vec{q}}{dt} - \dot{\vec{G}} &= (\vec{E} \times \vec{m}) + (\vec{B} \times \vec{p}) + e(\vec{B} \times \vec{r}_0). \end{aligned} \right.$$

Here \vec{G} , \vec{E} , \vec{M} , \vec{q} refer to the inner field; \vec{E} , \vec{B} represent the constant external field.

\vec{M} and \vec{q} are angular momentum and position of the centre of energy relative to the arbitrary origin. We introduce instead the corresponding quantities relative to the particle

$$(7, 11) \quad \begin{cases} \vec{M}' = \vec{M} - (\vec{r}_0 \times \vec{G}), \\ \vec{q}' = \vec{q} - \vec{r}_0. \end{cases}$$

If we restrict ourselves to the quasi-stationary case where \vec{G} , \vec{E} depend on \vec{v} in the same way as for free motion ($\vec{E} = 0$, $\vec{B} = 0$), then

$$(7, 12) \quad \vec{G} = E\vec{v}, \quad \dot{\vec{r}}_0 \times \vec{G} = \vec{v} \times \vec{G} = 0,$$

therefore

$$(7, 13) \quad \frac{d\vec{M}'}{dt} = \frac{d\vec{M}}{dt} - \left(\vec{r}_0 \times \frac{d\vec{G}}{dt} \right).$$

(7, 10) can be written

$$(7, 14) \quad \begin{cases} \frac{d\vec{M}'}{dt} = (\vec{B} \times \vec{m}) - (\vec{E} \times \vec{p}) + [\vec{r}_0 \times \{\vec{B} \times (e\vec{v} + \dot{\vec{p}})\}], \\ \frac{d\vec{E} \vec{q}'}{dt} = (\vec{E} \times \vec{m}) + (\vec{B} \times \vec{p}) + e(\vec{B} \times \vec{r}_0) - \vec{r}_0 [\vec{E} \cdot (e\vec{v} + \dot{\vec{p}})]. \end{cases}$$

The additional terms which are proportional to \vec{r}_0 have been omitted in Part I, just as the terms with $\dot{\vec{p}}$ in (7, 9). They have the following meaning: The "displacement current" $\dot{\vec{p}}$ is attacked by the magnetic field just as the convection current $e\vec{v}$, and modifies the orbit, conversely the orbit acts with a kind of centrifugal force on the angular momentum and the energy-centre. These effects can be neglected for slow motions (as done in I) if $\dot{\vec{p}}$ is supposed to vanish for $\vec{v} = 0$ (Kramers's assumption $\vec{p} = \vec{m} \times \vec{v}$); but here, in the general case, this is not allowed

8. Conclusion.

The equations (7, 9), (7, 14) are a generalisation of Kramers's equations, derived in I, to which they reduce for $\dot{\vec{p}}_0 = 0$. The new equations are self-consistent without imposing a restriction on the Lagrangian. This seems

satisfactory from the purely formal standpoint. But on the other hand the elementary particles occurring in nature (electrons, protons) have no electric rest-moment, as far as we know. If the classical treatment of the unitary theory has a meaning at all, it leads to the conclusion that point singularities are not the correct representation of the particles. The question whether there exist other possibilities will be considered later.

THE MEASUREMENT OF THE TRANSMISSION OF HEAT BY CONVECTION FROM INSOLATED GROUND TO THE ATMOSPHERE.

BY P K RAMAN

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Introduction

FOR more than six hours on a clear day in tropical and subtropical continental areas, the ground is often more than 15°C warmer than the air at a level of 4 ft above ground, and at the time of maximum ground-temperature, the excess may be as much as $25\text{--}35^{\circ}\text{C}$. This implies the transfer of a considerable amount of heat every day from the heated ground to the atmosphere and this process of convective heating plays a large part in determining the thermal properties of the air over these regions. A few attempts have been made by European workers^{1,2,3} to estimate the quantities of heat transferred to the atmosphere by convection in temperate regions. But quantitative measurements are few and the methods are often indirect. Dines² estimates the average daily addition of heat throughout the earth by convective processes to be 200 calories/cm². This includes the heat (150 cal/cm²) contributed by condensation of moisture. In the present paper is described a simple apparatus for determining the rate at which heat is transferred from dry ground to the atmosphere, the instrument was used to determine the quantity of heat transferred to the atmosphere by convection on a number of days in clear weather at Poona during the period, January-May 1935. The results of the open-air measurements are compared with those from laboratory experiments obtained by other workers and it is shown that a simple formula can be used for estimating the rate at which heat is transferred to the atmosphere from heated ground in terms of the surface temperature of the ground and the meteorologically measured quantities, temperature of air and wind-velocity at 4 ft.

As a problem of general ærodynamics, the subject of heat transfer from a hot body by convection to the surrounding fluid has been investigated by a number of workers, both experimentally and theoretically. When the fluid has no general movement, but has only internal movements arising from the differences of density caused by the contact of portions of the fluid

with the hot solid, the convection is called 'free' or 'natural'; when a general movement of the fluid is super-posed, the convection is called 'forced'. In the atmosphere natural convection is of comparatively less importance, as absolute calm is very rare, especially in the hot hours of the day. For theoretical calculations, the surface of the earth may be considered as a rough horizontal plane of infinite extent and the stream of fluid roughly parallel to the surface.

Apparatus and Method of Measurement

The apparatus used for measuring the rate of transfer of heat is similar in principle to that of the Angstrom's Pyrgeometer. A thin polished silver-plated constantan strip AB (Fig 1) is mounted between the ends of a pair

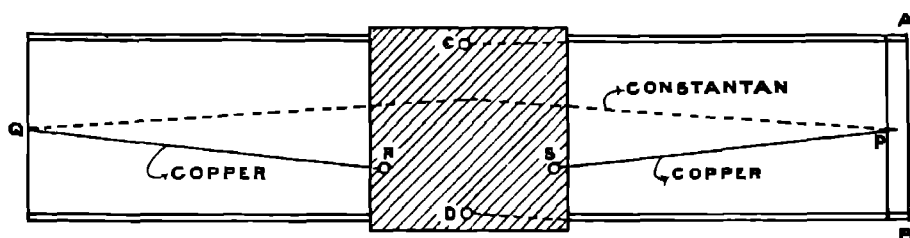


FIG. 1

of parallel copper rods (nickel-plated and polished) carried on a base of ebonite. The copper rods are connected to two terminals C and D. One junction P of a copper-constantan thermo-couple is placed in thermal contact with the centre of the surface of the strip AB; the other junction at Q being suitably mounted on silk fibres so that it can be placed in contact with the surface under investigation. The under-side of the constantan strip is lined with a layer of cork so that when placed on the ground it is thermally insulated from it. R and S are the terminals for connecting the thermo-couple to a suspended coil galvanometer. The strip can be heated electrically as required and the current measured on a calibrated ammeter. The convection apparatus was exposed in the open while the battery, electrical instruments, etc., were housed in an adjoining hut.

The measurements were made on clear days during the winter of 1935 at the Agricultural Meteorological Observatory at Poona which is situated in an open place well removed from buildings. On a selected plot of level ground the apparatus was placed with the under-surface of the strip thermally insulated from the ground and the junction Q in thermal contact with the soil surface. The upper surface of the strip was placed flush with the surface of the ground (but not actually touching it) so as to reduce the boundary effects to a minimum. The current required to be passed through the strip when it was at the same temperature as the soil surface was measured.

Because of turbulent wind movements a perfectly steady null position could not be obtained. The reading of the current was taken when the galvanometer oscillated symmetrically about its zero position.

When the strip is in thermal equilibrium with the surface of the ground it gains heat energy from the electric current passing through it, and from the radiation of the sun and the sky, it loses heat by long wave radiation and by convection. The convective loss which is equal to that of the surrounding ground can be evaluated if the gain and loss of heat due to the remaining factors can be determined.

The energy consumed for heating the strip can be calculated from the current i , the resistance R and the area A of the strip. Thus

$$H = Ki^2 = \frac{60 R}{AJ} i^2 \text{ gm cal./cm}^2 \text{ min} \quad \dots \quad (1)$$

To estimate the loss or gain of heat by radiation we require the effective absorptivity of the strip both for visible and for infra-red radiation. These were determined experimentally as below.

A Pyrheliometer of the Angstrom type was constructed with two strips of constantan cut from the same strip as was used for the convection instrument. One strip was kept with the original polish on and the other was given a thin uniform coating of lamp black. A series of measurements were taken with this Pyrheliometer with both the strips or the black strip alone successively exposed to direct solar radiation. From these the percentage of the incoming energy absorbed by the bright strip can be calculated. The average of a series of measurements showed that the bright strip absorbed 0.25 of the incident solar radiation. This same Pyrheliometer was used as a Pyrgeometer for measurements of nocturnal radiation and comparative observations taken with a standard Angstrom Pyrgeometer showed that the effective absorptivity of the bright strip was not appreciably different from 0.25 for thermal radiation also.

The heat transferred to the air from unit area of the strip in a unit of time by convection can be calculated as follows —

$$H = \frac{Ri^2}{AJ} + a\Sigma + a_1(s - \sigma T^4) \quad \dots \quad (2)$$

where

H is the heat transferred by convection in gm cal./cm.² min.,

i is the heating current in amperes,

R and A are the resistance and area of the strip respectively,

Σ solar and visible sky radiation on a horizontal surface in gm.cal./cm.² min.,

s atmospheric radiation (gm cal /cm² min.) obtained from the mean of observations with Angstrom's Pyrgeometer on the previous night,
 σT^4 the black body radiation (gm cal /cm² min) at the temperature T° Absolute of the ground at the time of observation , σ being the Stefan-Boltzmann constant,
 a and a_1 are the effective absorptivities of the strip for solar radiation and for long wave radiation respectively.

Measurements were also taken of the following elements before and after each reading with the convection apparatus :—

- (1) The temperature of the surface of the ground with a surface thermometer.
- (2) The temperature of the air above ground by an Assmann thermometer at about 1 cm above surface.
- (3) The temperature of the air at 4 ft. (from thermometer in Stevenson screen)
- (4) The wind-velocity at the two levels 1½ ft and 6 ft by Robinson cup anemometers
- (5) The radiation from the sun and the sky received on a horizontal surface at the time of each observation as read off from the Kipp and Zonen Solarigraph installed at the Observatory.

Results and Discussion

Measurements of heat loss from ground due to convection show considerable fluctuations especially when the excess temperature of the ground is more than 10° C Ordinarily, in winter and early hot season, the fluctuations are found to be greatest between the hours 10 and 14. Analysing the observations according to wind-velocity of 4 ft. above ground, the mean rates of loss of heat measured on different occasions are given in Tables I and II expressed as the ratio of the rate of loss of heat to the temperature difference between ground and air at 4 ft. For purposes of general application, it is necessary to find a formula that would fit the observations with a reasonable degree of accuracy In the analysis of the results of laboratory experiments made by different investigators M. Fishenden and O. A. Saunders⁴ have given the following formula for the rate of heat transmission under conditions of natural convection from a horizontal surface with colder air above :—

$$H = 0.38 \theta^{5/4} \frac{\text{British Thermal Units}}{\text{ft.}^2 \text{ hr.}} \quad \text{where } \theta \text{ is expressed in } ^\circ\text{F or}$$

$$H/\theta = 0.0036 \theta^{1/4} \frac{\text{Cal.}}{\text{cm.}^2 \text{ min. } ^\circ\text{C.}} \quad \dots \dots \dots (3)$$

In (3), θ is the difference of temperature between the surface and the air outside the 'boundary' layer. The thickness of this layer is very variable when the wind-velocity approaches zero, under laboratory conditions with surfaces of limited area, it is 0.5 to 2 cm. In the open air, temperature continues to decrease for much greater heights, although the largest falls take place within the first 1 cm. In calculating H/θ according to (3) in Table I, the difference between the temperature of the ground (T_g) and the temperature of the air at 4 ft. (T_4) has been used. Very near the ground, the fluctuations of temperature are very large and the difficulty of defining the height also is great when the reference surface is as rough as the ground. It was found that in calm weather during the hot hours of the day, the temperature difference at about 1 cm above ground was 1.5-1.6 times that at 4 ft. If in evaluating H/θ in column 3 of Table I, the difference of temperature between ground and air at 1 cm had been used, the calculated values would have been still smaller. For purposes of calculation it appears that we can take the temperature of the air at 4 ft level as the effective temperature of the air.

TABLE I.

θ °C.	H (observed)	H (calculated)
8.0	.066	.048
11.2	.086	.071
16.9	.184	.123
18.3	.148	.136

For forced convection, Jürges' laboratory experiments gave the following relation for the heat loss from a rough surface. The surfaces were copper plates 50 cm square placed in alignment with the walls of a duct through which air was blown by means of a fan. Jürges' relation for rough surfaces was taken as representing the best approach to natural conditions.

For velocities $v < 5$ metres per sec., $H/\theta = .0088 + .0059 v$. . . (4)
 where H is expressed in cal/cm² min, θ in degree Centigrade and v in metres/sec. The temperature and velocity of the air were presumably measured well outside the skin layer.

In Table II are grouped the mean values of H/θ for different values of v , measured in the open air at Poona and the values calculated according to

equation (4). The values of θ and v used in the calculation refer to air at 4 ft. above ground.

TABLE II.

v m/s	Mean H/θ observed	H/θ calculated according to (4)
0	·009	·0088
0·6	·016	·0123
0·9	·013	·0141
1·2	·018	·0159
1·5	·022	·0177
1·8	·020	·0191
2·4	·028	·0230
2·7	·027	·0247
3·0	·026	·0265
3·6	·031	·0300
3·9	·035	·0318
4·2	·033	·0336
4·8	·037	·0371

Velocities greater than 5 m/sec. were rarely experienced at 4 ft., but Jürges' relation for rough surfaces for these velocities takes the form

$$H/\theta = 0.011 v^{0.78} \quad \dots \quad (5)$$

K. Buttner, working in Tripolian Sahara, obtained the values 0·016 and 0·021 for H/θ for values of wind-velocity 0·8 to 1·5 m./sec. and 2 to 2·5 m./sec at $\frac{1}{2}$ metre height above ground

In Fig. 2 are plotted the curve of equation (4) and the individual observational values. It appears that on the whole, the equation gives an under-estimate for the actual amount of heat transferred by convection. We have, however, to remember the difference between the definitions of v and θ in the laboratory and open-air experiments. It is not easy to make a theoretically unexceptionable choice regarding the level at which v and θ

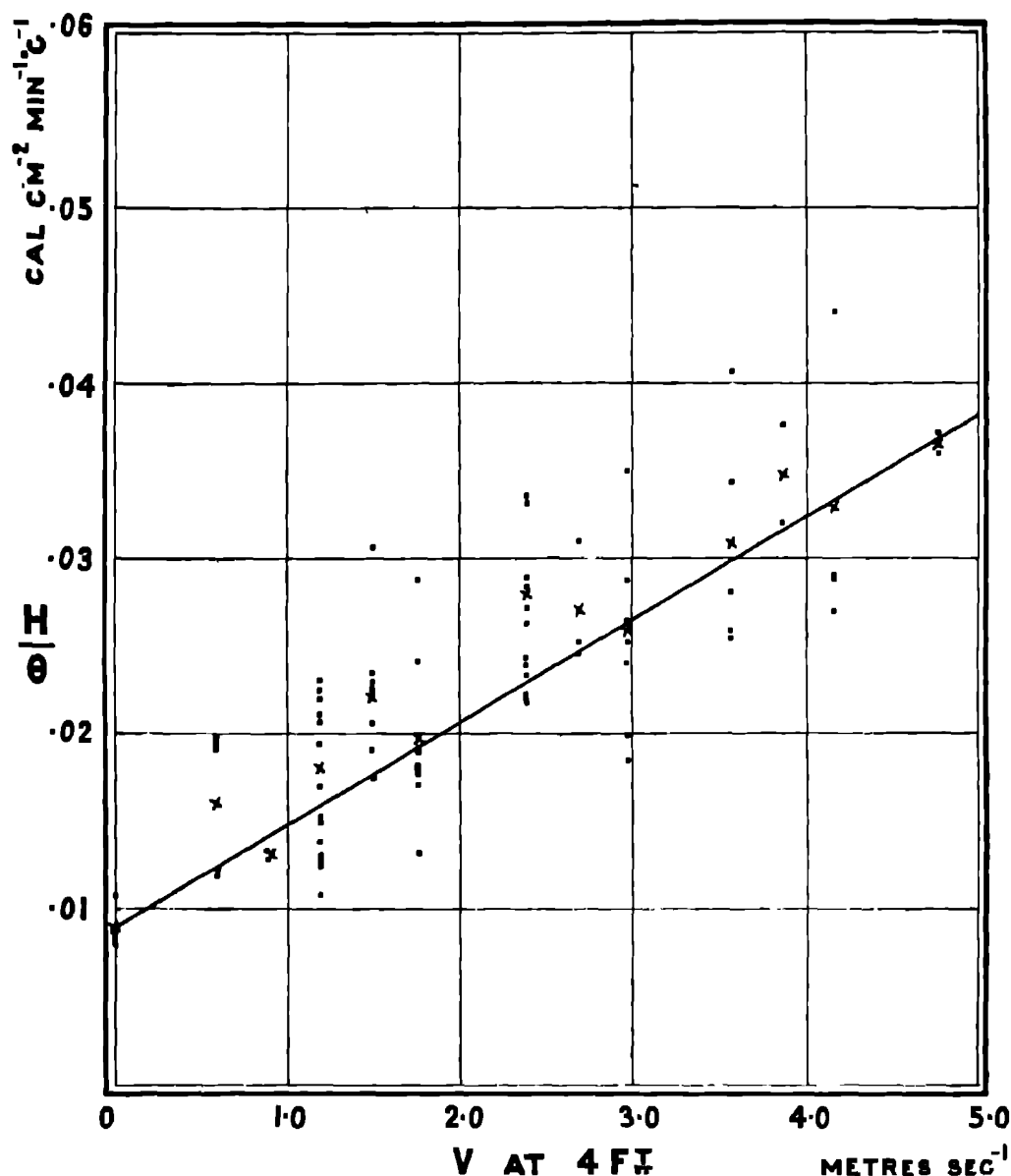


FIG. 2.

should be measured for open-air experiments. Both these quantities vary rapidly with height immediately above the ground. The four-foot level* was chosen partly because it is well outside the region of largest fluctuations and partly because this is the level at which meteorological observations are usually taken, so that the results can later be extended to other places and conditions. To obtain a general estimate of the quantities involved, it appears that Jürges' formula can be employed, if θ and v are taken to refer

* Actually, the wind-velocity was measured at $1\frac{1}{2}$ feet above ground by means of a cup anemometer and converted to that at 4 feet by means of the relation $v_{3/2}/v_4 = 0.75$.

to 4 ft. level. Further measurements with an improved apparatus are projected for a more rigorous test of the applicability of the formula.

In Fig. 3 is shown a curve showing the variation of heat transmission by convection at different times on 2. 2. 35. The curve represents the values calculated by (4) and the marked points the measured values. The integrated loss of heat by convection on this day comes to be 175 calories. The

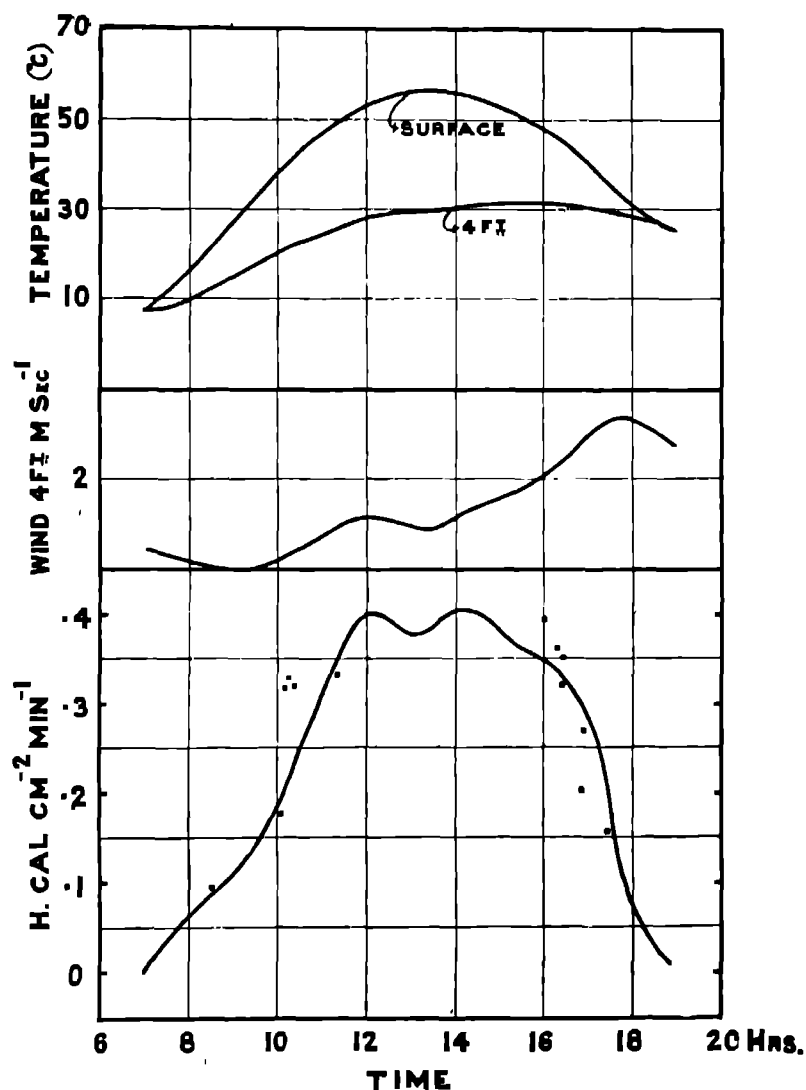


FIG. 3.

integrated heat loss on a number of days in the period February to May ranged from 175 to 340 cal per day. In the region of sub-tropical highs in which Poona is situated in this season, we may take the average daily quantity of heat transferred by convection to the atmosphere on clear days to be about 250 calories. When the ground is dry, this will appear directly in the form of increase of temperature. When we are considering moist

ground or sea areas, the energy will go into the atmosphere partly in the form of latent energy of water-vapour. In dry land areas, the effect of this daily transference of heat to the lower atmosphere would be to raise the temperatures of the lower layers and set up a large lapse-rate in the first few kilometres of the atmosphere. Assuming that all the heat added by convection in one day goes to increase the temperature of the first 3 km. of the atmosphere, the resulting average increase of temperature will be

$$\frac{250}{0.241 \times 1.0 \times 10^{-4} \times 10^5 \times 3} \text{ or } 3^{\circ}.4 \text{ C.}$$

Rise of temperature will, however, cause an increase of radiation of heat from the atmospheric layer and this, operating both day and night, would reduce the actual rise of temperature.

Cold air is sometimes brought down into lower latitudes during winter in the wake of western depressions, and this often spreads over the Deccan. The cold spells which follow are, however, brought to an end within two or three days when there is no fresh advent of cold air from the north. It is evident that the heat gained by the atmosphere by convection from the insolated ground will itself be sufficient to bring this about in two or three days.

In conclusion, the author desires to express his grateful thanks to the Director-General of Observatories for the facilities given and to Dr. K. R. Ramanathan and Dr I. A. Ramdas for their guidance and help during the progress of this investigation. His best thanks are also due to Mr. G. Chatterji, Meteorologist-in-Charge, Upper Air Observatory, Agra, for kindly sending a reel of thin constantan strip which was used in this investigation. The experiments are being continued with improved apparatus.

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STUDIES IN THORIUM PHOSPHATE GELS.

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THORIUM phosphate gels were first prepared by Satya Prakash¹ by directly mixing solutions of thorium nitrate and potassium phosphate. A precipitate which is first obtained disappears on shaking and gives rise to a more or less opaque solution. This when kept for some time becomes clear and sets to a firm transparent gel. According to him the precipitated thorium phosphate is peptised by the hydrogen and thorium ions present in the gel-forming mixtures and this process is greatly accelerated by shaking. Later on, the colloidal solution of thorium phosphate coagulates and the particles get hydrated and in course of time the whole mixture sets to a solid looking mass imbibing within itself all the liquid present in the mixture, provided suitable concentrations of solutions of thorium nitrate and potassium phosphate are employed.

It has been found by the authors that thorium phosphate gels can be easily prepared if a solution of phosphoric acid instead of that of potassium phosphate is used. Only a slight precipitate is obtained when solutions of thorium nitrate and phosphoric acid are mixed and it quickly disappears on shaking. The resulting solution is quite transparent and sets to a firm transparent gel.

In the following an attempt has been made to investigate systematically the factors that affect the time of setting of these gels. Consequently the behaviour of thorium and hydrogen ions and the effect of temperature and of the addition of extra amounts of electrolytes and non-electrolytes to the gel-forming mixtures has been investigated.

Experimental

Kahlbaum's purest thorium nitrate and phosphoric acid whose purity was tested, were used. A number of trials indicated that 6 per cent solution of thorium nitrate and 2N solution of phosphoric acid gave very good

¹ *J. Indian Chem. Soc.*, 1929, 6, 587.

gels when different volumes of these solutions were mixed. Hence these solutions were used throughout the investigation

A known amount of thorium nitrate solution was taken in one test tube and in another a known amount of the solution of phosphoric acid together with some distilled water so that when the two solutions were mixed the total volume of the mixture was 10 c.c. The mixture was then slightly shaken for about 15 seconds and was then poured into a tube which was gently inverted twice and set aside. This method of mixing was followed throughout the investigation.

The time required by the gel-forming mixture to reach a state when it did not flow out of the tube and showed a firm meniscus on inverting it was taken to be the time of setting of the gel. The accuracy of these measurements was increased by repeating the observations several times and each time disturbing the mixture as few times as possible during setting. This enabled the determination of the time of setting fairly accurately. The results obtained are given in Tables I and II in which

Q = grams of thorium nitrate in 10 c.c. of mixture ,

X = equivalent of phosphoric acid in the mixture , and

T = time of setting in minutes.

TABLE I.

Q	0.18	0.42	0.36	0.39
X	T	T	T	T
0.24 N	8	ppt. settles down ; no gel.	ppt.	ppt.
0.22 N	15	7.5	ppt.	ppt.
0.20 N	32	20	6	ppt.
0.18 N	105	49	23	2
0.16 N	233	162	88	18
0.14 N	about 24 hrs.	about 12 hrs.	185	42.5
0.12 N	does not set : a clear sol.	a clear viscous sol : does not set.	about 14 hrs.	91

TABLE II.

X	0.18	0.16	0.14	0.12
Q	T	T	T	T
0.48	105	233	about 24 hrs	Clear viscous sol: no gel.
0.42	49	162	about 12 hrs.	„
0.36	23	88	185	about 14 hrs.
0.30	2	18	42.5	91
0.24	no gel: ppt.	no gel: ppt.	6.5	22.5
0.18	„	„	ppt.	2
0.12	„	„	„	ppt.
0.06	„	„	„	„

All the gels mentioned in the tables were absolutely transparent throughout the entire process of gelation and the gel-forming mixtures were acidic.

It will be seen that for the same thorium nitrate content of the mixture the time of setting decreases as the concentration of phosphoric acid in the mixture is increased while for the same concentrations of phosphoric acid it increases with an increase in the amount of thorium nitrate in the mixture.

It may be pointed out that gels can be obtained only within the range of concentrations of thorium nitrate and phosphoric acid given in the above tables. If the amount of phosphoric acid in the mixture is increased or decreased beyond these limits a curd (or a gelatinous precipitate) or a perfectly transparent solution which never sets to a stiff gel, is obtained. The reverse happens in the case of thorium nitrate. A more or less viscous and transparent loose mass is obtained when the amount of thorium nitrate in the mixture is more and a curd when it is less than the amounts given in the above tables.

Effect of Temperature

Prakash² has found that the time of setting of thorium phosphate gels decreases as the setting takes place at a higher temperature. Table III gives

² *J. Indian Chem. Soc.*, 1932, 9, 192.

the results obtained with gels prepared in the manner mentioned above. These results are in agreement with the conclusions of Prakash.

TABLE III.

$$X = 0.16 N$$

Temp.	Q	0.30	0.36	0.42	0.48
50°C.	T	6	17	61	170
40°C.	T	10	38	130	192
28°C.	T	18	88	182	233

It was noticed that gels prepared at higher temperatures were cloudy and the cloudiness disappeared gradually after some time. They were also stiffer than those prepared at lower temperatures. These observations indicate that the gels prepared at higher temperature consist of bigger aggregates which are not highly hydrated.

Effect of Electrolytes

Electrolytes are known to cause the coagulation of a sol. In a gel-forming mixture this is brought about by the electrolytes formed due to the metathetical reaction. If extra amounts of electrolytes are added to this mixture, the coagulation process may be hastened. Thus Prasad and Hattiangadi³ found that the time of setting of the silicic acid gel-forming mixtures is decreased as a larger quantity of electrolytes is added to them. In the following the effect of the addition of some salts, acids and sodium hydroxide on the setting of thorium phosphate gels has been described. For this purpose different quantities of the solutions of the electrolytes were added to fixed amounts of phosphoric acid solutions and the requisite amount of distilled water was added to make up the total volume of the gel-forming mixture to 10 c.c. In the following tables A represents the normality of the electrolytes in the gel-forming mixtures.

(a) *Effect of salts*—The salts used were chlorides of sodium and barium and sodium sulphate.

³ *J. Indian Chem. Soc.*, 1930, 7, 341.

TABLE IV.

NaCl

$$Q = 0.36$$

X	A	0	0.2 N	0.4 N	0.6 N	0.8 N	1.0 N
0.12 N	T (hrs.)	14	10	6.5	5	3.5	1.5
0.14 N	T (min.)	200	155	117	84	58	36
0.16 N	T (min.)	88	57	37	32	28	17

TABLE V.

$$Q = 0.36 \quad X = 0.16 \text{ N}$$

BaCl ₂			Na ₂ SO ₄		
A	T	Remarks	A	T	Remarks
0	88	transparent gel	0	88	transparent gel
0.005 N	63	translucent gel	0.02 N	60	„
0.010 N	56	„	0.04 N	16	translucent gel
0.015 N	50	„	0.06 N	1	opaque
0.020 N	41	completely opaque gel	0.08 N	—	disjointed hydrates

It is clear that the time of set decreases as the amount of salts in the gel-forming mixtures is increased.

The gels obtained in the presence of sodium chloride were quite transparent from the beginning of gelation till they set, but slight turbidity developed when the amount of sodium chloride was fairly large. No transparent gels were obtained in the presence of BaCl₂ and Na₂SO₄ when concentrations equivalent to NaCl were used but only a gelatinous precipitate separated out. However, with very small amounts of these electrolytes translucent and opaque gels were obtained.

(b) *Effect of sodium hydroxide.*—1 N sodium hydroxide solution was used.

TABLE VI.

$$Q = 0.36$$

X	0.16 N		0.18 N		0.20 N	
A	T	Remarks	T	Remarks	T	Remarks
0	88	transparent gel	20	transparent gel	0	transparent gel
0.02 N	102	"	26	turbid mixture	7	turbid mixture
0.05 N	108	} gel-forming mixture turbid	35	"	—	—
0.10 N	360		105	"	14	translucent gel, ppt separates and settles down
0.20 N	—	no gel, ppt slowly settles down	—	no gel, ppt separates and settles down	—	—

TABLE VII.

$$X = 0.18 N$$

Q	0.30		0.36		0.42	
A	T	Remarks	T	Remarks	T	Remarks
0	1	transparent gel	20	transparent gel	72	transparent gel
0.02 N	3	gel-forming mixture turbid	26	turbid mixture	90	"
0.05 N	5	"	35	"	120	"
0.10 N	7	"	105	"	about 8 hrs	"
0.15 N	15	translucent gel	140	"	—	—
0.20 N	—	ppt separates and settles down	—	No gel, ppt. separates and settles down	—	transparent viscous mass, ppt. separates and settles down

While preparing the gels it was noticed that they were turbid and the turbidity persisted in some gels till the setting point and disappeared in others just when they were about to set. Also the opacity of these mixtures increased with an increase in the concentration of NaOH. Thus in the presence of limited amounts of NaOH both transparent and opaque gels were obtained. Some of the set opaque gels became clear on keeping for some time while others did not undergo any change in their opacity. The

gels obtained by Satya Prakash⁴ by using potassium phosphate were similar to those obtained by us in the presence of NaOH. These gels, however, do not look quite homogeneous.

It will be seen that the time of set increases as the amount of NaOH in the gel is increased. On testing the various gel-forming mixtures by various indicators it was found that they were fairly acidic. The pH of the mixture with no amount of NaOH was nearly 1.2 and this increased to nearly 2.5 as different amounts of NaOH were added to them. If larger amounts of NaOH were added, no gel but an amorphous precipitate was formed.

(c) *Effect of acids*—4 N nitric and hydrochloric acids and 0.5 N sulphuric acid were used for the purpose. As the behaviour of nitric acid was found to be similar to that of hydrochloric acid, only the results with the latter acids are given

TABLE VIII.
Effect of Hydrochloric Acid
X = 0.14 N

A	Q = 0.30		A	Q = 0.36	
	T	Remarks		T	Remarks
0	42.5	transparent gel	0	185	transparent gel
0.2 N	29	"	0.08 N	70	"
0.4 N	40	"	0.20 N	30	"
0.6 N	about 12 hrs	"	0.40 N	22	"
0.8 N	20	opaque	0.60 N	50	"
1.0 N	17	"	0.72 N	21	slightly opalescent
1.2 N	12	transparent	1.0 N	7	opaque gel
			1.2 N	—	hydrated flakes

It is clear that with increasing amounts of hydrochloric acid the time of setting at first diminishes, reaches a minimum, then suddenly increases and again diminishes till a second minimum is reached. With the addition of sulphuric acid, however, the time of setting at first increases and then begins to decrease and the first minimum found with hydrochloric acid is

⁴ *Loc. cit.*

TABLE IX.
Effect of Sulphuric Acid
 $Q = 0.36$

A	X = 0.14 N		X = 0.16 N	
	T	Remarks	T	Remarks
0	185	transparent gel	88	transparent gel
0.01 N	255	loose and translucent gel	110	loose and translucent gel
0.02 N	310	„	90	„
0.03 N	220	„	58	„
0.04 N	71	„	18	„
0.05 N	35	„	8	„
0.06 N	14	„	4	„
0.07 N	6	„	1.5	„
0.08 N	3	„	< 1	„
0.09 N	1	„	—	no gel; the ppt. separates and settles down slowly
0.10 N	< 1	„	—	—

not observed. It may correspond to some concentration of the acid lower than 0.01 N which has not been used in the investigation. With further increase in the amount of the acid, *i.e.*, more than that corresponding to the minimum, at first hydrated flakes are formed and then a clear solution is obtained which shows no turbidity nor any increase in viscosity on keeping.

Effect of Non-electrolytes

The rôle of non-electrolytes in their action towards colloidal solutions is not yet clearly understood. Several examples are known in which they act either as coagulating or inhibiting agents. Billitzer⁵ found that a

⁵ *Zeit. Phys. Chem.*, 1903, **45**, 312.

negatively charged platinum sol could be sensitized, discharged or even changed into a positive sol by the addition of suitable amounts of alcohol. Prasad and Hattiangadi⁶ found that the addition of alcohols decreases the time of setting of the alkaline silicic acid gels and increases that of the acidic ones. In the following the effect of the addition of methyl, ethyl and propyl alcohols and glycerine on the time of setting of thorium phosphate gels has been described. The addition of the non-electrolytes was done in the same manner as that of electrolytes.

TABLE X
Q = 0.36 X = 0.16 N

Amount of non-electrolyte	Methyl alcohol	Ethyl alcohol	Propyl alcohol	Glycerine
	T	T	T	T
0	88	88	88	88
1.0 c.c.	104	115	97	4.5 hrs.
2.0 c.c.	125	175	178	7 „
3.0 c.c.	230	213	about 5 hrs.	about 24 hrs.

It will be seen that the setting of gels is retarded by the presence of the non-electrolytes and this effect is enhanced as the amount of the non-electrolytes is increased.

Gels prepared with larger amounts of alcohols were turbid in the beginning, but after some time the turbidity slowly disappeared and transparent gels were obtained. Glycerine seems to have a considerable retarding influence. All gels obtained in the presence of glycerine were perfectly transparent from the beginning to the end of gelation but the structure of these gels was extremely loose.

Discussion of Results

The observations described above can be used to define the conditions which govern the formation of thorium phosphate gels. When solutions of thorium nitrate and phosphoric acid are mixed, they react and thorium phosphate and nitric acid are formed; all the gel-forming mixtures, therefore, show an acid reaction. A slight precipitate is obtained because thorium phosphate dissolves only in concentrated solution of acids and is insoluble

⁶ *J. Indian Chem. Soc.*, 1929, 6, 991.

in dilute ones. The insolubility and the appearance of the precipitate are necessary, for when this precipitate goes over to the colloidal state on shaking, it supersaturates the solution with the gelling substance and in accordance with the views of von Weimarn creates circumstances favourable for the formation of a gel. The gel formation is, of course, determined by the hydration tendency of thorium phosphate and the agglomeration tendency of the micelles.

An increase in temperature (i) decreases the hydration tendency and increases the agglomeration tendency of the micelles and (ii) may also decrease the peptising capacity of the peptising ions. Both these effects cause the gel to set early with larger aggregates at a higher temperature. If the temperature is, however, further increased, no gel but only a precipitate should be obtained. This is probable as it was observed that in mixture, containing 0.30 g of thorium nitrate and 0.18 N phosphoric acid, the precipitate obtained remained suspended for a long time before a homogeneous mass was formed.

The addition of extra amounts of salts also increases the agglomeration tendency of the gelling substance and decreases the hydration tendency since such an addition hastens the coagulation of the micelles more so if ions of higher valency are employed. Thus the gels set early and are turbid.

H⁺-ions seem to be very effective in peptising thorium phosphate. The first decrease in the time of setting observed in Table VIII is an evidence of this effect since with an increase in the H⁺-ion concentration in the mixture the rate of peptisation of the precipitate is also increased. Reverse happens when the H⁺-ion concentration is decreased by the addition of sodium hydroxide (*cf.* Tables VI and VII). This effect of the H⁺-ions is supported by the observation that the precipitate in mixtures containing the amount of the acid corresponding to the first minimum gets peptised without shaking.

With an increase in the concentration of the acid beyond that corresponding to the first minimum the increased peptising action of the H⁺-ions increases the degree of dispersity of the micelles and delays the setting. After a certain concentration of the acid which imparts the maximum charge to the micelles any further addition increases the concentration of the coagulating ion and decreases the time of set; at some concentration the coagulation becomes very rapid and a precipitate is formed. The gels corresponding to the range between the maximum and the second minimum are opalescent and this supports the view that further addition of acids increases the agglomeration tendency. The coagulating effect of the anions is also apparent from the fact that gels of greater opalescence are obtained as the concentration of sulphuric acid beyond that corresponding to the maximum is

increased. Further, due to the increased coagulating effect of the divalent sulphate ion the concentrations of sulphuric acid employed are ten times smaller than those of hydrochloric acid

Prasad and Hattiangadi⁷ have also observed that with concentrated acids a second minimum time of set is obtained in the gelation of silicic acid. Holmes⁸ has also made a similar observation in the gelation of silicic acid by sulphuric and hydrochloric acids. He has pointed out that the second minimum is caused by the dehydrating influence of the concentrated acids, but Prasad and Hattiangadi have shown that it is the coagulating effect of the anion which comes more into play after the density of charge on the colloidal particles of the gelling substance has attained its maximum value.

Thorium phosphate is peptised to a fairly large extent by thorium ions as well. This is seen from the fact that all mixtures in Tables I and II contain thorium nitrate in excess of that required for the complete precipitation of thorium phosphate. Consequently if the amount of thorium nitrate in mixtures containing the same concentration of phosphoric acid is increased, the degree of dispersity of the colloidal particles increases and they take longer time to form bigger aggregates in order to set to a stiff gel. If the amount of thorium nitrate in the mixtures is increased or decreased beyond the limits indicated in the tables, the amount of the peptising ion in the mixture is either too great or too small and hence, as observed, either a viscous mass or a curd, respectively, is obtained.

If the concentration of phosphoric acid is increased beyond the limit given in the tables, the amount of thorium phosphate formed is increased and the concentration of thorium ions falls. Thus the gelling substance does not reach a sufficiently high degree of dispersity and supersaturation and a curd is obtained. If the concentration of phosphoric acid is lower than that indicated in the tables no gel but a viscous mass is formed for (i) the dispersity of the precipitate is very high as there are a large number of thorium ions to peptise a small amount of the precipitate and (ii) the amount of the precipitate (number of micelles) is insufficient to enmesh the whole of the liquid.

These observations, therefore, support the suggestion of Fernau and Pauli⁹ that for the formation of a gel it is necessary that the concentration of the micelles must be high. Their second suggestion that the micelles

⁷ *Loc. cit.*

⁸ *J. Phys. Chem.*, 1918, 22, 510.

⁹ *Biochem. Zeit.*, 1915, 70, 426; *Kolloid Zeit.*, 1917, 20, 20.

should be hydrophillic in nature and should remain so upon coagulation is satisfied by the chemical nature of thorium phosphate which has a great tendency for hydration.

The action of alcohols and glycerine is similar to that observed by Prasad and Hattiangadi¹⁰ for the acidic silicic acid gel-forming mixtures as these gels also take a longer time to set in the presence of alcohols. These authors concluded from their observation that alcohols exert a protective influence on the positively charged sols by causing an increase in the density of charge on the particles. In the present case an increase in the density of charge and thereby in the degree of dispersity of thorium phosphate is caused by alcohols probably by effecting an increase in the adsorption of H⁺-ions by the micelles. The first appearance of the turbidity in the presence of alcohols caused by the insolubility of thorium phosphate in alcohol-water mixtures and its disappearance after a certain time leads one to believe that the above assumption is justifiable. In the presence of glycerine thorium phosphate gets dispersed to such a high degree that aggregates big enough to give a rigid structure are not formed.

¹⁰ *Loc. cit*

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART IV.

Generalised Theory.

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1. Introduction.

IN Part III¹ of this series of papers, we considered the Doppler effects and coherence phenomena among the diffracted components of light emerging from a rectangular cell of a medium traversed by supersonic waves perpendicular to the direction of the propagation of the incident plane wave of light. We showed, in the case of a progressive supersonic wave, that the n th order diffraction component which is inclined at an angle $\sin^{-1}(-n\lambda/\lambda^*)$ to the direction of propagation of the incident light has the frequency $\nu - n\nu^*$, where ν and λ denote the frequency and the wave-length of the incident light while ν^* and λ^* correspond to those of the sound wave. In the case of the diffraction of light by a standing sound wave, we got the interesting result that in any even order, radiations with frequencies $\nu \pm 2r\nu^*$, ($r = 0, 1, 2, \dots$), would be present while in any odd order, radiations with frequencies $\nu \pm \overline{2r+1}\nu^*$, ($r = 0, 1, 2, \dots$), would be present. These results give a satisfactory interpretation of the coherence phenomena among the diffraction components observed by Bär². In the following, we show that our previous results remain valid even if we consider a *general* periodic supersonic wave and that they can be derived in a simple and direct fashion. We have also presented in the following, some general considerations of the problem on hand.

2. Doppler effect and coherence phenomena

The partial differential equation governing the propagation of light in a medium with time-variation and space-variation in its refractive index is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \left[\frac{\mu(x, y, z, t)}{c} \right]^2 \frac{\partial^2 \psi}{\partial t^2}$$

¹ C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci. (A)*, 1936, 3, 75.

² R. Bär, *Helv. Phys. Acta*, 1935, 8, 591.

if the frequency of the time-variation of $\mu(x, y, z, t)$ is very slow compared to the time-variation of the wave-function of light. This would be so in the case of the propagation of light in a medium filled with sound waves for the frequency of the variation of $\mu(x, y, z, t)$ corresponds to the frequency of the sound waves present in the medium, which is negligible compared to the frequency of light.

If we choose our axes of reference such that the X-axis points to the direction of the propagation of the plane sound waves and the Z-axis points to the direction of the propagation of the incident plane wave of light, we could ignore the dependence of ψ on y and write the differential equation as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} = \left[\frac{\mu(x, t)}{c} \right]^2 \frac{\partial^2 \psi}{\partial t^2}$$

If $\mu(x, t)$ did not depend on time, ψ would have had the only time factor $\exp(2\pi i \nu t)$ where ν is the frequency of the incident light. If we consider the time variation of $\mu(x, t)$, we can write ψ as given by

$$\psi = \exp[2\pi i \nu t] \phi(x, z, t)$$

where $\phi(x, z, t)$ varies slowly in time compared to $\exp[2\pi i \nu t]$. On the consideration that $\nu^* \ll \nu$, we can show that

$$\left| 4\pi \nu \frac{\partial \phi}{\partial t} \right| \ll \left| 4\pi^2 \nu^2 \phi \right| \quad \text{and} \quad \left| \frac{\partial^2 \phi}{\partial t^2} \right| \ll \left| 4\pi^2 \nu^2 \phi \right|.$$

With these considerations, we can consider the differential equation

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = - \frac{4\pi^2}{\lambda^2} \{\mu(x, t)\}^2 \phi$$

and obtain ψ by the equation

$$\psi = \exp[2\pi i \nu t] \phi(x, z, t).$$

As the sound waves which travel along the X-axis are periodic in space and time, we can regard $\mu(x, t)$ to be also periodic in x and t with the same periods in space and time. It should be noticed that we do not restrict $\mu(x, t)$ to be simply periodic in x and t but it may be a general periodic function of x and t , amenable to Fourier Analysis. Thus

$$\mu(x + p\lambda^*, t) = \mu(x, t)$$

and

$$\mu(x, t + p/\nu^*) = \mu(x, t)$$

where p is any integer.

If we consider the differential equation in which $\mu(x, t)$ has the above properties, we see that $\phi(x, z, t)$ should also be periodic in x and t with the same periods in the case we are considering. That is,

$$\phi(x + p\lambda^*, z, t) = \phi(x, z, t)$$

and

$$\phi(x, z, t + p/\nu^*) = \phi(x, z, t)$$

Hence we can write the double-Fourier expansion of $\phi(x, z, t)$ as

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{rs}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t}$$

Progressive Sound Waves —In the case of the progressive waves travelling along the positive direction of the X-axis, we have the property that

$$\mu(x + \rho \lambda^*, t) = \mu(x, t - \rho / \nu^*)$$

where ρ is any number. Thus

$$\phi(x + \rho \lambda^*, z, t) = \phi(x, z, t - \rho / \nu^*) \quad \dots \quad \dots \quad (1)$$

Using the double-Fourier expansion, we can write (1) as

$$\begin{aligned} & \sum \sum f_{rs}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t} e^{2\pi i \nu \rho} \\ &= \sum \sum f_{rs}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t} e^{-2\pi i s \rho} \quad \dots \quad \dots \quad \dots \end{aligned} \quad (2)$$

Comparing the Fourier coefficients on each side of (2), we get

$$f_{rs}(z) e^{2\pi i \nu \rho} = f_{rs}(z) e^{-2\pi i s \rho}$$

This could be true only if

$$f_{rs}(z) = 0 \quad \text{when } r \neq -s \quad \dots \quad \dots \quad (3)$$

The condition (3) restricts the number of terms in the Fourier expansion of ϕ , so that

$$\phi(x, z, t) = \sum_{-\infty}^{\infty} f_r(z) e^{2\pi i r x / \lambda^*} e^{-2\pi i r \nu^* t}$$

Thus

$$\phi(x, z, t) = \sum_{-\infty}^{\infty} f_r(z) e^{2\pi i r x / \lambda^*} e^{2\pi i (\nu - r \nu^*) t} \quad \dots \quad \dots \quad (4)$$

If one considers the diffraction effects of $\psi(x, z, t)$ given by (4), it is fairly obvious that the n th order diffraction component will be inclined at an angle $\sin^{-1}(-n\lambda/\lambda^*)$ with the incident beam of light and will have the frequency $\nu - n\nu^*$ and the relative intensity expression $|f_n(z)|^2$

Standing Sound Waves —In the case of standing waves, we have the property that

$$\mu\left(x + \frac{p\lambda^*}{2}, t\right) = \mu\left(x, t \pm \frac{p}{2\nu^*}\right), \quad p \text{ an integer,}$$

so that

$$\phi\left(x + \frac{p\lambda^*}{2}, z, t\right) = \phi\left(x, z, t \pm \frac{p}{2\nu^*}\right) \quad \dots \quad \dots \quad (5)$$

If we use (5) in the double Fourier expansion of ϕ we get

$$\begin{aligned} & \sum \sum f_{rs}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t} e^{\pi i r p} \\ &= \sum \sum f_{rs}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t} e^{\pi i s p} \quad \dots \quad \dots \quad \dots \end{aligned} \quad (6)$$

Comparing the Fourier coefficients in (6), we get

$$f_{rs}(z) e^{\pi i r p} = f_{rs}(z) e^{\pi i s p}$$

This means that $f_{rs}(z)$ is zero unless r and s are both even integers or odd integers.

Returning now to the Fourier expansion of ϕ , we could write it as

$$\begin{aligned}\phi(x, z, t) = & \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r, 2s}(z) e^{2\pi i 2rx/\lambda^*} e^{2\pi i 2sv^*t} \\ & + \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r+1, 2s+1}(z) e^{2\pi i (2r+1)x/\lambda^*} e^{2\pi i (2s+1)v^*t}\end{aligned}$$

Thus

$$\begin{aligned}\psi(x, z, t) = & \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r, 2s}(z) e^{2\pi i 2rx/\lambda^*} e^{2\pi i (\nu + 2sv^*)t} \\ & + \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r+1, 2s+1}(z) e^{2\pi i (2r+1)x/\lambda^*} e^{2\pi i (\nu + 2s+1)v^*t} \quad \dots \quad (7)\end{aligned}$$

If one considers the diffraction effects of $\psi(x, z, t)$ given by (7), it will be quite easy to see that the diffraction orders could be classed into two groups, one containing the even ones and the other odd ones; any even order contains radiations with frequencies, $\nu, \nu \pm 2\nu^*, \dots, \nu \pm 2r\nu^*, \dots$, and any odd order contains radiations with frequencies, $\nu \pm \nu^*, \nu \pm 3\nu^*, \dots, \nu \pm (2r+1)\nu^*, \dots$

3. The case when the disturbance in the medium is simple harmonic.

If we suppose that the variation in the refractive index of the medium is simple harmonic along the X-axis, it can be represented as

$$\mu(x, t) = \mu_0 + \mu \sin 2\pi(\nu^*t - x/\lambda^*)$$

in the case of a progressive wave, while it will be of the form

$$\mu(x, t) = \mu_0 - \mu \sin(2\pi x/\lambda^*) \sin(2\pi \nu^*t)$$

in the case of a standing wave, where $\mu(x, t)$ is the refractive index of the medium at height x and at time t , μ_0 is the constant refractive index of the medium when there is no sound wave and μ is the *maximum variation* of the refractive index from μ_0

Progressive Wave — To obtain the wave function for the emerging wave-front of light, we have to solve the differential equation

$$\begin{aligned}\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2} = & - \frac{4\pi^2}{\lambda^2} \{\mu(x, t)\}^2 \phi \\ = & [A + \frac{B}{2i} \{e^{i(bx-\epsilon)} - e^{-i(bx-\epsilon)}\}] \phi \quad \dots \quad (8)\end{aligned}$$

where $b = 2\pi/\lambda^*$, $\epsilon = 2\pi\nu^*t$, $A = -4\pi^2\mu_0^2/\lambda^2$ and $B = 8\pi^2\mu_0\mu/\lambda^2$ omitting the second order term with coefficient μ^2 .

We have shown in the previous section that ϕ can be developed as a Fourier series in x and t as

$$\sum_{-\infty}^{\infty} f_r(z) e^{2\pi i r x / \lambda^*} e^{-2\pi i r v^* t}$$

or

$$\sum_{-\infty}^{\infty} f_r(z) e^{i r b x} e^{-i r \epsilon} \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

Substituting the Fourier series (9) in the differential equation (8) and comparing the Fourier coefficients we obtain the equation

$$\frac{d^2 f_n}{dz^2} - (A + b^2 n^2) f_n = \frac{B}{2i} (f_{n-1} - f_{n+1})$$

Putting $f_n(z) = \exp(-i u \mu_0 z) \phi_n(z)$ where $u = 2\pi/\lambda$ we obtain

$$\frac{d^2 \phi_n}{dz^2} - 2i u \mu_0 \frac{d\phi_n}{dz} - b^2 n^2 \phi_n = -\frac{Bi}{2} (\phi_{n-1} - \phi_{n+1})$$

Putting $z = (2\pi\mu)^{-1} \lambda \xi$, we obtain

$$\mu^2 \frac{d^2 \phi_n}{d\xi^2} - 2i \mu_0 \mu \frac{d\phi_n}{d\xi} - \frac{n^2 \lambda^2}{\lambda^{*2}} \phi_n = -\mu_0 \mu i (\phi_{n-1} - \phi_{n+1})$$

As μ_0 , being the refractive index of the medium, is in the neighbourhood of unity and μ is in the neighbourhood of 10^{-5} , we can omit the first term on the left hand side and consider the differential equation

$$2 \frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = \frac{i n^2 \lambda^2}{\mu_0 \mu \lambda^{*2}} \phi_n.$$

If there were no term on the right hand side, ϕ_n would be the Bessel Function $J_n(\xi)$ or $J_n(2\pi\mu z/\lambda)$ satisfying the required boundary conditions. This follows as a consequence of Sonine's³ theorem which gives that if

$$2 \frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = 0,$$

then ϕ_n could be developed as a series in Bessel Functions as

$$\phi_n(\xi) = \phi_n(0) J_0(\xi) + \sum_1^{\infty} [\phi_{n-s}(0) + (-)^s \phi_{n+s}(0)] J_s(\xi)$$

Setting the boundary conditions that

$$\phi_0(0) = 1 \text{ and } \phi_s(0) = 0, \quad s \neq 0$$

we get

$$\phi_n(\xi) = J_n(\xi).$$

If n is not too great and $\lambda^2/\lambda^{*2}\mu$ is small, we can approximate

$$\phi_n(\xi) \approx J_n(\xi) = J_n\left(\frac{2\pi\mu z}{\lambda}\right)$$

³ N. Nielsen, *Handbuch der theorie der Cylinderfunktionen*, p. 286 (1904 edition).

If the cell is bound by $z = L$, at the emerging face, it will be easy to see that the relative intensity of the n th order diffraction component would be $J_n^2 (2\pi\mu L/\lambda)$

The case of the standing wave—In this case we have to write $\phi(x, z, t)$ as given by

$$\begin{aligned}\phi(x, z, t) &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r, 2s} e^{2\pi i 2rx/\lambda^*} e^{2\pi i 2sy^*t} \\ &\quad + \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{2r+1, 2s+1} e^{2\pi i \overline{2r+1}x/\lambda^*} e^{2\pi i \overline{2s+1}y^*t} \\ &= \sum_{-\infty}^{\infty} g_r(z, t) e^{2\pi i rx/\lambda^*} \quad \dots \quad \dots \quad \dots \quad (10)\end{aligned}$$

Substituting (10) the differential equation for ϕ and comparing the coefficients, we obtain

$$\frac{\partial^2 g_n}{\partial z^2} - \frac{4\pi i \mu_0}{\lambda} \frac{\partial g_n}{\partial z} - \frac{4\pi^2 n^2}{\lambda^{*2}} g_n = \frac{4\pi^2 \mu_0 \mu \sin \epsilon}{\lambda^2 i} (g_{n-1} - g_{n+1})$$

Putting $z = (2\pi\mu)^{-1}\lambda\xi$ we obtain

$$\mu^2 \frac{\partial^2 g_n}{\partial \xi^2} - 2i\mu_0 \mu \frac{\partial g_n}{\partial \xi} - \frac{n^2 \lambda^2}{\lambda^{*2}} g_n = -\mu_0 \mu \sin \epsilon (g_{n-1} - g_{n+1}).$$

Under the same considerations as in the previous paragraph, we will have to solve the equation

$$2 \frac{\partial g_n}{\partial \xi} - \sin \epsilon (g_{n-1} - g_{n+1}) = \frac{in^2 \lambda^2}{\mu_0 \mu \lambda^{*2}} g_n.$$

If n is not too great and $\lambda^2/\lambda^{*2}\mu$ is small we can approximate

$$g_n(\xi, \epsilon) \approx J_n(\xi \sin \epsilon) = J_n\left(\frac{2\pi\mu z}{\lambda} \sin 2\pi\nu^* t\right).$$

But we have shown in Part III,¹ that

$$\begin{aligned}J_{2n}(v \sin \epsilon) &= \sum_{-\infty}^{\infty} (-)^r J_{n-r}(v/2) J_{n+r}(v/2) e^{i2r\epsilon} \\ J_{2n+1}(v \sin \epsilon) &= -i \sum_{-\infty}^{\infty} (-)^r J_{n-r}(v/2) J_{n+r+1}(v/2) e^{i2r+1\epsilon}.\end{aligned}$$

Hence,

$$\begin{aligned}\psi(x, z, t) &\approx \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} (-)^r J_{r-s}(v/2) J_{s+r}(v/2) e^{2\pi i 2rx/\lambda^*} e^{2\pi i (\nu+2s\nu^*)t} \\ &\quad - i \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} (-)^r J_{r-s}(v/2) J_{s+r+1}(v/2) e^{2\pi i \overline{2r+1}x/\lambda^*} e^{2\pi i (\nu+\overline{2s+1}\nu^*)t}\end{aligned}$$

If one considers now the diffraction effects due to this emerging wave-front at $z = L$, it can be seen that an even order, say $2n$, contains radiations with frequencies $\nu \pm 2r\nu^*$, ($r = 0, 1, 2, \dots$), the relative intensity of the $\nu \pm 2r\nu^*$

sub-component being $J^2_{n-r}(\pi\mu L/\lambda)$ $J^2_{n+r}(\pi\mu L/\lambda)$ and an odd order, say $2n+1$, contains radiations with frequencies $\nu \pm \overline{2r+1}\nu^*$, ($r = 0, 1, 2, \dots$), the relative intensity of the $\nu \pm \overline{2r+1}\nu^*$ sub-component being $J^2_{n-r}(\pi\mu L/\lambda)$ $J^2_{n+r+1}(\pi\mu L/\lambda)$

4. Summary

The essential idea that the phenomenon of the diffraction of light by high frequency sound waves depends on the corrugated nature of the transmitted wave-front of light, pointed out by the authors in their first paper, has been developed on general considerations in this paper. The results in this paper can be summarised as follows:—

(1) If progressive sound-waves travel in a rectangular medium normal to two faces and the direction of propagation of a plane beam of incident light, the incident light will be diffracted at the angles given by $\sin^{-1}(-n\lambda/\lambda^*)$ and the light belonging to the n th order will have the frequency $\nu - n\nu^*$.

(2) If the sound waves are stationary, the incident light will be diffracted at the angles given by $\sin^{-1}(-n\lambda/\lambda^*)$, an even order would contain radiations with frequencies, ν , $\nu \pm 2\nu^*$, $\nu \pm 4\nu^*$, \dots , $\nu \pm 2r\nu^*$, \dots , and an odd order would contain radiations with frequencies $\nu \pm \nu^*$, $\nu \pm 3\nu^*$, $\nu \pm 5\nu^*$, \dots , $\nu \pm \overline{2r+1}\nu^*$, \dots .

(3) A differential-difference equation has been obtained for the amplitude function of the diffracted orders whose approximate solution is satisfied by the Bessel Functions already obtained by the authors in their previous papers

MOLECULAR CLUSTERING IN LIQUID FATTY ACIDS.

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1. Introduction.

It is well known that the light scattered transversely by a liquid is not in general perfectly polarised, but shows a defect of polarisation which is characteristic of each liquid. This partial depolarisation arises from the fact that in general, we are dealing with two types of scattering in an ordinary liquid, one type called the density scattering arising from the molecular disarray in the medium and consequent local fluctuations in its optical density, and the other type called the orientation scattering arising from the varying orientations of the molecules which are anisotropic. The density scattering is completely polarised, while the orientation scattering is depolarised to the extent of $6/7$. Due to the combined effect, the light scattered transversely is depolarised to some extent depending upon the proportion in which the two types of scattering exist. The above idea is based on the supposition that the scattering in a liquid is completely molecular in origin, *i.e.*, the ultimate scattering particles are the molecules of size small compared with the wave-length of light. Using incident unpolarised light, as also light polarised with electric vector respectively vertical and horizontal, different measures of the state of polarisation of the transversely scattered light are obtained, namely, ρ_u , ρ_v and ρ_h corresponding to the three cases. For any liquid where the scattering is really molecular in origin

$$\rho_h = 1 \text{ and } \rho_u = 2\rho_v/(1 + \rho_v) \quad \dots \quad \dots \quad \dots \quad (1)$$

and consequently it is not necessary to measure all the three quantities separately. But once the above condition is not fulfilled, *i.e.*, when the particles in the medium can no longer be identified with the individual molecules but only with molecular clusters or aggregates, ρ_h does not have its limiting value unity, but is definitely less than 1 and the simple relation (1) between ρ_u and ρ_v given above will no longer be satisfied. Consequently it will be quite insufficient to measure ρ_u alone. In such a case it has already been shown by the author¹ that there is a simple general relation connecting

¹ R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 1, 782.

the three quantities ρ_u , ρ_v and ρ_h , namely,

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \quad \dots \quad (2)$$

Relation (1) is a special case of this very general relation. In any scattering experiment, therefore, it is highly necessary to make comparative studies of the intensity and state of polarisation of the scattered light with the incident light in the three different states of polarisation, in order to get a correct idea of the state of dispersion of the scattering particles in the medium. Any departure of the value of ρ_h from unity will at once indicate an appreciable size of the scattering particles.

The above method has been successfully employed by the author in the case of liquid mixtures in the neighbourhood of the critical solution temperature.² The observations furnished for the first time positive evidence for the existence of large clusters in liquid mixtures not only at the critical solution temperature but also at temperatures considerably above that temperature. It was, therefore, considered desirable to extend this sensitive method to the case of highly associated liquids in order to know more about the state of dispersion of the molecules in them. In the present investigation, a detailed study of the scattering of light in the first four members of the fatty acids, namely, formic acid, acetic acid, propionic acid and normal butyric acid, at different temperatures with the incident light in the three different states of polarisation. The experimental results have obviously an important bearing on some of the anomalies observed in these acids by the earlier investigators on light scattering.

2. Experimental Details

Merck's extra pure sample of formic acid was further purified by redistillation over pure anhydrous boric oxide (free from silicon) in an all-glass distillation apparatus. Extra pure glacial acetic acid (Merck's) was used as such without further chemical purification, whereas propionic acid and butyric acid were also purified by distillation over phosphorus pentoxide. The pure liquids were contained in small sealed bulbs about 2" in diameter of clear and homogeneous glass. They were rendered dust-free by repeated slow distillation *in vacuo* in the usual way before they were sealed off. Particular care was taken to see that the liquids were absolutely free from dust. The bulb containing the liquid to be examined was kept immersed in distilled water contained in a rectangular brass vessel provided with three glass windows for the incident and the scattered beams. The bath was heated electrically. The source of light and the optical arrangement were

² R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 1, 915; 1935, 2, 221.

the same as those employed in the earlier investigations of the author. Extraneous light, if any, coming out in the direction of observation was cut off by suitably blackening the bulb and the vessel and making observations at a distance of about 10" from the cell.

On inserting a double-image prism in the track of the incident beam and one in the track of the scattered beam (both of them oriented in such a way that the upper image as seen through them corresponded to vertical vibrations), it was found that in the case of acetic and formic acids the lowest image out of the four images observed was distinctly brighter than either of the middle two. The depolarisation factors ρ_u , ρ_v and ρ_h of the transversely scattered light were measured as usual with a double-image prism and a nicol using respectively incident unpolarised light, incident light polarised with vibrations vertical and horizontal. The value of ρ_h was found to be unusually less than its limiting value of 100%. The observations were repeated with the four fatty acids at various temperatures. The relative intensity of scattering in these liquids at different temperatures was determined by using a photo cell in conjunction with a valve bridge amplifier, in the manner described in the author's earlier paper.³ The results are tabulated below

The value of ρ_h is found to be less than 100% in the case of the first two members at lower temperatures. This raises the question whether the observed value of ρ_h is genuine or is due to some errors in the experiment. Dust particles, if any, in the liquid would vitiate the results very much. But in the present experiment this question does not arise at all since the liquids used were completely free from dust. Another source of error is fluorescence. It was found that none of the liquids studied was sensibly fluorescent.

TABLE I.

Liquid	Nature of the container	ρ_h %	ρ_v %	ρ_u %
Acetic acid	Pyrex cross temp. = 25° C.	90	30.5	49.5
	Spherical bulb temp. = 25° C.	91	30	50
Formic acid	Pyrex cross temp. = 25° C.	88	31	51
	Spherical bulb temp. = 25° C.	87	30.5	49

³ R. S. Krishnan, *Proc. Ind. Acad. Sci., (A)*, 1935, 2, 221.

TABLE II.

(a) *Formic acid (Bulb as container)*

Temperature $t^{\circ}\text{C.}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn (1) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
25	87	30.5	49	17	50	1.2
41	90	27	47	13	15	1.1
55	91	24	40	39	40.5	1.05
70	93	21.5	36	35	37	1.0 (assumed)
90	100	18.5	30	32	32	1.2

TABLE III.

(b) *Acetic acid (M.P. = 15°C) (Bulb as container)*

Temperature $t^{\circ}\text{C.}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn (1) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
20	91	33	52.5	50	52	1.3
25	91	31	50	47	50	1.3
45	93	23.5	40.5	38	40	1.25
60	95	22	38	36	37.5	1.2
80	96.5	19.5	33	32.5	33.5	1.0 (assumed)
93	100	18	29	30	30	1.0

TABLE IV. (c) *Propionic acid (Bulb as container)*

Temperature $t^{\circ}\text{C}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn (2) %	Relative intensity of scattering
25	100	27	42.0	42.5	1.00 (assumed)
42	100	23.5	37	38	1.05
60	100	19.5	33	33	1.11
75	100	17	28.5	29	1.25
85	100	16	27	27	1.33

TABLE V. (d) *Normal Butyric acid (Bulb as container)*

Temperature $t^{\circ}\text{C}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
25	100	20	34.5	33	1.08
45	100	19	32.5	32	1.00 (assumed)
60	100	16	27.5	27.5	1.00
74	100	13.5	24	24	1.08
88	100	11	18	20.5	1.19

where ρ_u and ρ_v are defined as the ratio of the intensity of the horizontal component to that of the vertical component of the scattered light and ρ_h is defined as the ratio of the intensity of the vertical component to that of the horizontal component. Column 5 in Tables II and III gives the values of ρ_u calculated from the observed values of ρ_v using the simplified relation (1). The column 6 in these tables gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h using relation (2). It is seen that these calculated values of ρ_u are decidedly in better agreement with the observed values showing thereby that equation (1) is no longer true for these two acids.

Moreover, fluorescence, if any, would never have the effect of lowering the value of ρ_h . Another possible source of error in the measurement of depolarisation is the convergence of the incident beam. In the present case the diameter of the long focus lens employed for focussing the light emerging out of the square aperture was 4 cms. The light was brought to a focus at a distance of about 52 cms. from the lens. Consequently the angle of convergence is equal to $1/13$ th of a radian. This angle was further reduced to $3/52$ radian inside the medium by the liquid in the rectangular cell. According to Gans⁴ and Ananthakrishnan⁵ the convergence correction for ρ_u is $\omega^2/8$, where ω is the angle of convergence, and for a convergence angle of $3/52$ radian, the correction would be 0.0004. This is negligibly small compared with the high depolarisation of the fatty acids and consequently it can be neglected. The corrections for ρ_v and ρ_h are also likewise negligibly small.

In order to be sure that the observed values of the depolarisation were not vitiated by any irregularity in the walls of the container, a pyrex cross was made. Each of its arms was 3" long and $1\frac{1}{2}$ " in diameter. Strain free pyrex plates were fused on to the ends. This cross was connected to a flask. Acetic and formic acids were distilled dust-free into the cross from the flask, one after the other. The measurements of depolarisation were repeated at the room temperature with the cross as container. The readings taken with the bulb and the cross as containers are given in Table I. The two corresponding readings are quite in agreement within the limits of experimental error.

3. Discussion of Results.

The most striking characteristic of acetic and formic acids is that ρ_h is only about 90% at 25° C, showing thereby that the scattering in these liquids is no longer purely molecular in origin, but should be attributed to the presence of molecular clusters. The average size of these aggregates is not small compared with the wave-length of light. This fact is also evidenced from the accuracy with which the data satisfy the theoretical relation (2). As the temperature is increased, the value of ρ_h increases steadily and finally attains its limiting value of 100%. From this it naturally follows that the degree of association and the size of the molecular aggregates formed depend very much on temperature. The lower the temperature, the greater is the association and larger is the size of the clusters. In the case of propionic and butyric acids ρ_h is found to be always equal to 100%.

⁴ R. Gans, *Phys. Zeits.*, 1927, **28**, 661.

⁵ R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 133.

These two acids may also be associated to some extent, but the degree of association is not so great as to be detected by the present experimental technique. In spite of the high value of ρ_u for formic acid, the value of ρ_h is least for this. From this it directly follows that of all the fatty acids, formic acid is the most highly associated one and the degree of association diminishes as the number of carbon atoms increases.

The intensity of scattering in acetic and formic acids shows some anomalies. On the basis of molecular theory, the orientation scattering in a liquid which depends on the number of molecules per unit volume, does not vary appreciably with rise of temperature, whereas, the density scattering which is directly proportional to the absolute temperature T and the compressibility β increases with rise in temperature. Therefore, the total intensity of scattering in a liquid where the scattering is truly molecular, should rise with temperature. This fact is well illustrated in the case of propionic and butyric acids. On the other hand in the case of the first two members of the fatty acid series, the intensity of scattering diminishes at first with rise in temperature up to about 80°C . and above this temperature it begins to increase. This also shows that at the ordinary temperatures the scattering in these two liquids is not in accordance with the molecular theory, but is influenced by the presence of large molecular aggregates.

In this connection it would be interesting to mention the anomalies observed by the earlier investigators on light scattering in these fatty acids. I. Ramakrishna Rao⁶ has determined the depolarisation of the transversely scattered light and the optical anisotropy of a large number of organic vapours, and in almost all the cases he finds that the molecular anisotropy in the liquid state is definitely less than that in the vapour state. The significant exceptions are formic acid and acetic acid where the anisotropy in the liquid state is greater than that in the vapour state. He has calculated the anisotropy from the observed value of the depolarisation using the modified formula of Ramanathan.⁷ The values of the anisotropy δ for these four fatty acids are given in the accompanying Table VI.

S. Ramachandra Rao⁸ has studied the variations of intensity and depolarisation factor of the transversely scattered light in the case of a large number of liquids. He finds that in almost all liquids the optical anisotropy as calculated from the depolarisation values using Ramanathan's modified formula, increases with rise in temperature. But in the case of acetic acid

⁶ I. Ramakrishna Rao, *Ind. Journ. Phys.*, 1927, 2, 61.

⁷ K. R. Ramanathan, *Ind. Journ. Phys.*, 1926-7, 1, 401.

⁸ S. Ramachandra Rao, *Ind. Journ. Phys.*, 1928, 3, 1.

TABLE VI.

No.	Liquid	δ in the vapour state	δ in the liquid state
1	Formic acid ..	33.3×10^{-3}	17×10^{-3}
2	Acetic acid ..	25.9×10^{-3}	36.2×10^{-3}
3	Propionic acid	23.5×10^{-3}	20.1×10^{-3}
4	Butyric acid ..	15×10^{-3}	16.5×10^{-3}

it is found that the optical anisotropy decreases from a value of 31×10^{-3} at 30°C to 19×10^{-3} at 120°C . and above that temperature it increases steadily in the normal way. Formic acid was not included in his investigation as the values of its compressibility at different temperatures were not available. On the basis of molecular association this anomalous behaviour could be easily accounted for. The depolarisation factor arises not only from the actual anisotropy of the individual scattering particles, but also from their finite size. Consequently the anisotropy as calculated from the observed values of ρ_{\parallel} without applying correction for the finite size of the molecular aggregates, is bound to give a higher value. Besides, the aggregates formed may also possess a higher effective anisotropy than the individual molecules themselves and consequently the anisotropy in the liquid state at the ordinary temperatures which is an aggregate of molecular clusters may be higher than that in the vapour state. This increase in the effective anisotropy will itself give rise to a higher value for the depolarisation factor ρ_{\parallel} and also for the total intensity of scattering. As the liquid is heated up, the degree of association diminishes and the anisotropy decreases tending to attain its normal in the state of no association.

The present investigation furnishes for the first time definite experimental evidence for the existence of molecular clusters, of size not small compared with the wave-length of light in highly associated fatty acids. Further experimental work with other highly associated liquids and also with supercooled liquids is in progress.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt, F.R.S., N.L., for his continued interest and guidance during the progress of this investigation.

5. Summary.

The variations in intensity and depolarisation factor of the transversely scattered light have been studied in detail in the case of the first four fatty

acids, namely, formic acid, acetic acid, propionic acid and normal butyric acid, with the incident light in the three different states of polarisation, namely, unpolarised, horizontally polarised and vertically polarised. In the case of formic and acetic acids at the room temperature the depolarisation factor ρ_h was found to be about 90% when the incident light is polarised with vibrations horizontal. This observation furnishes for the first time definite experimental evidence for the existence of large molecular aggregates in these highly associated liquids, of size not small compared with the wave-length of light.

ρ_h increases with rise in temperature and at about 90° C it attains its limiting value of 100% in these two acids. The intensity of scattering also at first diminishes with rise in temperature in these two cases, contrary to the molecular theory of light scattering. It is shown that molecular association is distinctly the cause for the extraordinary behaviour of formic and acetic acids in the initial stages. Propionic and normal butyric acids do not show such anomalies.

DEFORMATION FREQUENCIES IN THE RAMAN SPECTRA OF LINEAR MOLECULES: ACETYLENE.

BY S BHAGAVANTAM

AND

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Received February 8, 1936

1 Introduction

THE fundamental vibrations of a linear molecule may be divided into two different types, *viz.*, the valency vibrations and the deformation vibrations. If the molecule possesses a centre of symmetry a further sub-division may be effected under the headings (i) totally symmetrical and (ii) antisymmetrical vibrations (Mecke, 1931). Of these various types, we may expect the total symmetric ones of both the valency and deformation vibrations to be 'Raman-active'. It must, however, be mentioned that the selection rules regarding the rotational structure differ very considerably in the two cases (Placzek, 1934). For valency vibrations we should expect a strong Q branch accompanied by O and S branches ($\Delta J = \pm 2$) and numerous examples of this type have already been found in the Raman spectra of gases like CO_2 , N_2O , etc. On the other hand, a deformation vibration should consist of only an extremely feeble Q branch accompanied by both O and S branches ($\Delta J = \pm 2$) and P and R branches ($\Delta J = \pm 1$) of normal intensity. No examples of this type have yet been experimentally observed in Raman spectra. Acetylene gas constitutes a very favourable case from this point of view. In this paper, is obtained and described a particularly intense Raman spectrum of this substance showing a pair of Raman bands at $\Delta \nu 600$ arising from a deformation vibration. The structure of this band agrees satisfactorily with the theoretical predictions.

2 The Normal Vibrations of the Acetylene Molecule.

The normal vibrations of the acetylene molecule have been discussed in detail by Mecke (*loc cit*) and by Sutherland (1935) and are represented diagrammatically in Fig. 1.

In the description of the diagram π stands for 'parallel' or valency oscillations and δ for 'perpendicular' or deformation oscillations. s and a stand for symmetric and anti-symmetric types respectively. It will be noticed

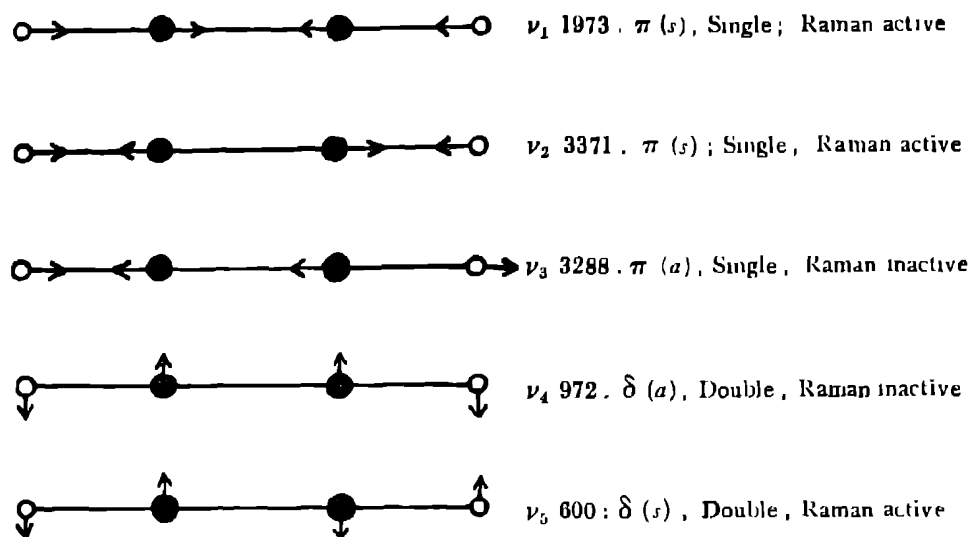


FIG. 1.

that of the three 'Raman-active' oscillations two are of the valency type and have already been observed in the Raman spectrum of acetylene gas (Bhagavantam, 1931). The third one is a deformation oscillation and has not yet been recorded in the Raman spectrum. From a detailed study of the combination bands appearing in the infra-red absorption spectrum of acetylene, Mecke and Sutherland have however deduced that its value should be about 600.

3. Raman Spectrum of Acetylene

Using a 2-prism glass spectrograph, the Raman spectrum of acetylene gas is obtained at a pressure of 18 atmospheres by giving an exposure of about 28 days. The picture is reproduced in the plate accompanying this paper. The pair of bands at about $\Delta\nu$ 600 excited both by λ 4046 and λ 4358 and recorded here for the first time are marked with arrows. It is proposed to interpret these as the unresolved O P and R S branches of the total symmetric deformation oscillation for which the Q branch is of negligible intensity. Measurements of the individual lines are contained in Table I (see next page).

The values given below the Table for ν_1 and ν_2 are the mean figures and are in good agreement with those reported earlier (Bhagavantam, 1931). It may also be noted that the mean of the two bands excited by λ 4358 is 617 whereas the mean of the corresponding bands excited by λ 4046 is 613. In view of the breadth of the bands the discrepancy is not very much and an average figure of 615 is assigned for ν_5 . The very faint line with a shift of 1941 wave numbers is to be attributed to the isotopic molecule $C_{12}C_{13}H_2$. This aspect is being investigated in greater detail by extending it to similar

TABLE I.
Raman Spectrum of Acetylene.

Wave-length	Intensity	Exciting line	Frequency
4768.4	10	4358	1972
4686.3	3	4046	3372
4606.0	0	4358 (?)	1233
4484.8	1 <i>b</i>	4358	646
4473.3	1 <i>b</i>	„	589
4435.0	1	4077	1974
4397.8	10	4046	1973
4391.7	0	„	1941
4179.2	1	3663	3372
4168.0	1	3654	3368
4162.2	2	3650	3370
4151.0	0 <i>b</i>	4046	639
4145.2	0 <i>b</i>	„	587
3948.7	3	3663	1975
3938.7	3	3654	1972
3933.4	5	3650	1973

$$\nu_1 = 1973 \text{ (10)}, \quad \nu_2 = 3371 \text{ (3)}; \quad \nu_3 = 615 \text{ (0)} \\ 1941 \text{ (0)}.$$

molecules such as ethylene and will be dealt with by one of us in a later communication. There is, however, another very weak but a definite line at $\lambda 4605 \cdot \lambda 0$ which, if attributed to $\lambda 4358$, gives a frequency shift of 1233. The origin of this is not clear

4 Discussion of Results

The most outstanding feature of the present investigation is the pair of bands at about $\Delta \nu 600$. It is suggested that they represent the maximum

of the unresolved rotational wings accompanying the total symmetric deformation oscillation of acetylene. The following points constitute the evidence in favour of such a suggestion.

The mean position of the bands corresponds to a frequency shift of 615 cm^{-1} which is in agreement with the figure derived indirectly from infrared absorption.

In a deformation vibration, we should expect the Q branch to be of negligible intensity in comparison with the O, P, R and S branches and this is confirmed.

The separation of the maxima is 57 cm^{-1} for the pair of bands excited by $\lambda\ 4358$ and 52 cm^{-1} for those excited by $\lambda\ 4046$. The former figure, which is more reliable, is in excellent agreement with the theory. In Fig 2, the

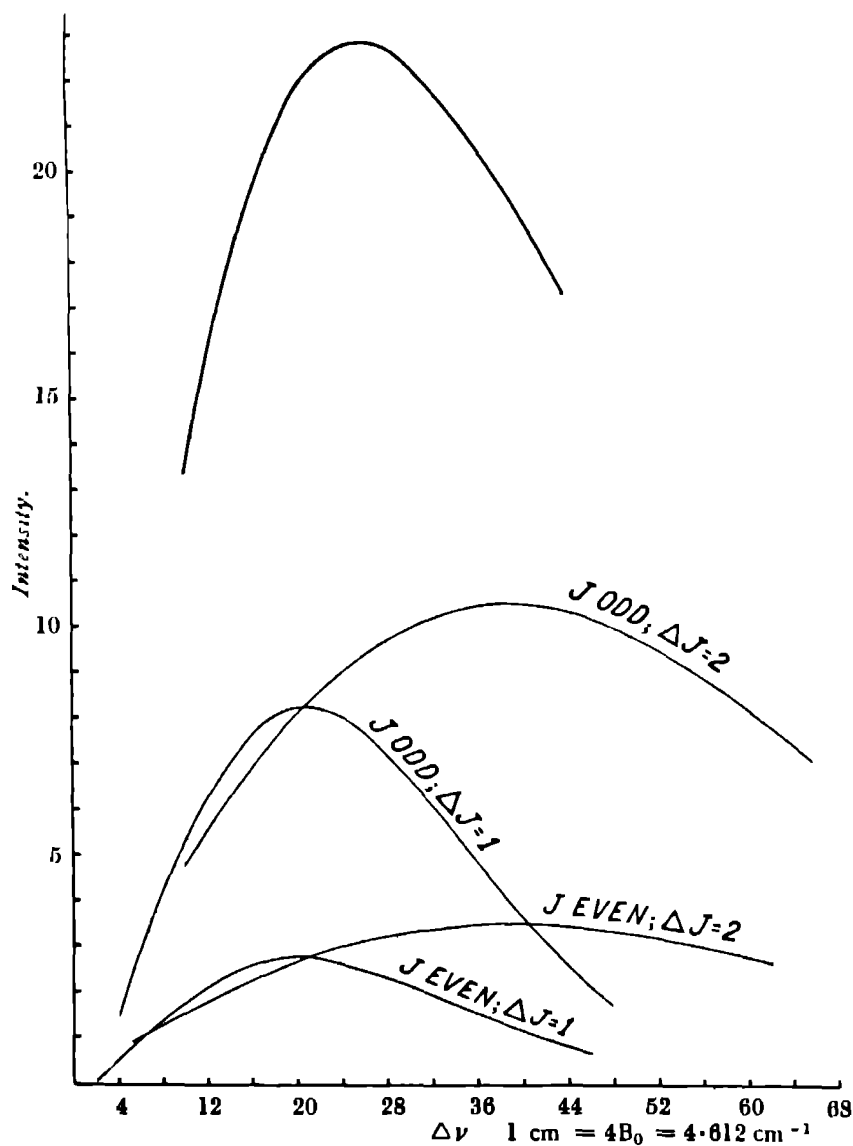
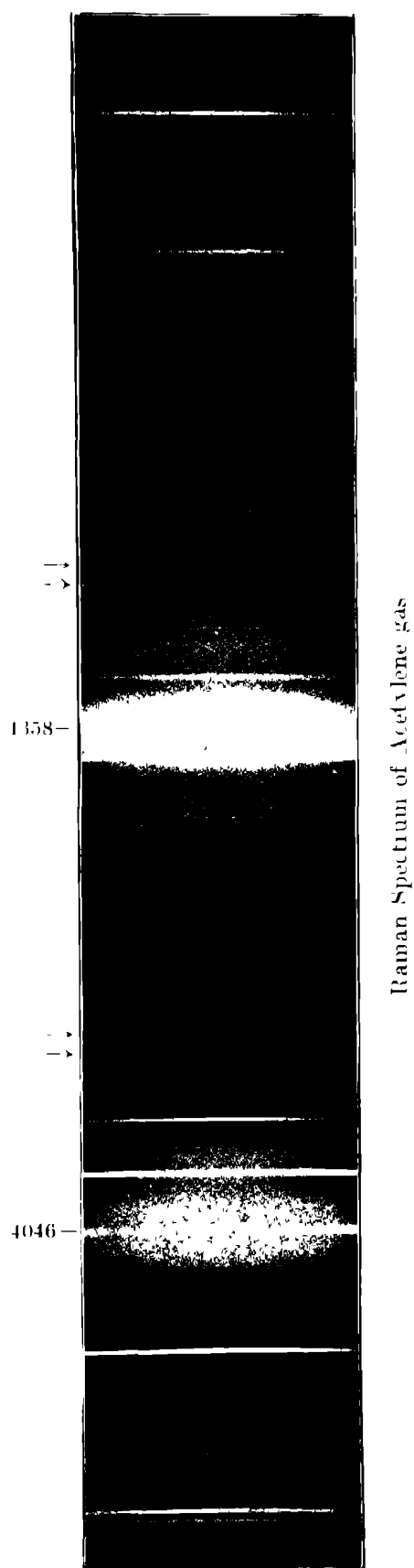


FIG. 2.



thin curves represent various branches that are to be expected on the Stokes side which in the unresolved state add up to give the aggregate band denoted by the thick line. The maxima of this aggregate band is fairly sharp and occurs at a distance of about 29 wave numbers from the centre or the missing Q branch so that the distance between the maxima should be 58 cm^{-1} which is in good agreement with the observation. In drawing the curves of Fig 2, it is assumed that the moment of inertia of the acetylene molecule is $24 \times 10^{-40}\text{ gm. cms.}^2$ and the odd rotational states are given a statistical weight 3 times as large as that given to the even rotational states. Calculations are carried out for a temperature of 30°C. on the basis of expressions given by Placzek

5 Summary

Two new bands at $\Delta\nu$ 589 and 646 have been recorded in the Raman spectrum of acetylene gas by giving a long exposure. These are interpreted as the maxima of the unresolved O, P, R and S branches of the total symmetric deformation vibration of the acetylene molecule. The negligible intensity of the Q branch and the observed separation of about 57 wave numbers between the bands are in accordance with such an interpretation. The frequency shift of about 615 corresponding to the mean position of the bands is in good agreement with the value deduced from the infra-red absorption for the frequency of this oscillation.

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INTENSITIES IN THE BANDS OF THE VIOLET CYANOGEN SYSTEM.

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Introduction.

THE application of Maxwell-Boltzmann distribution to vibrational levels in a band system has yielded very interesting results in many cases. The Franck-Condon theory of maximum transitions examined in relation to different functions expressing the nuclear potential energy of a diatomic molecule in a given electronic state gives different results which require to be verified by experiment. For this reason the subject of vibrational intensities in band spectra has assumed a great importance.

The violet bands of cyanogen form a system which is associated with violet glow when a carbon arc is struck in air. Other methods of exciting these bands are (a) active nitrogen, (b) electric furnace and (c) cyanogen gas burning in flame. The method of carbon arc in air has been chosen here on account of the easy occurrence of the bands and its nearer approach to conditions of thermal equilibrium.

In a paper by Ornstein and Brinkman,¹ one of the aspects, namely, of temperature by intensity measurements in this system, has been studied by the authors. In order to tackle the problem in all aspects and in view of the recent systematic work on gross intensities in some band systems, a thorough investigation of these bands was undertaken and the results are presented in this paper.

For the purposes of this paper, only the peak intensities near the heads of unresolved bands will be taken. Sufficient justification for taking the unresolved bands has been provided by Johnson and Tawde² and by Johnson and Dunston³ in recent papers. This is further supported by the work of Ornstein and Brinkman¹ who have proved by measurements that peak intensities near the heads are in the ratio of the sum of intensities of all the lines into which the band is resolved.

Experimental.

The technique of intensity measurements is the same as that indicated in previous papers^{2,3,4} in which further references relevant to the subject

can be found. The carbon arc was run at 3 amps on 100 volts, the arc length being on an average 8 mm. The band system was photographed on Hilger E₁ spectrograph having quartz system, along with the intensity marks taken with a step-slit having 8 elements. For this, a standard lamp of known energy distribution was used. The calibration of the lamp was done on Hilger quartz double monochromator of the Government Chemical Laboratory, London. The plates used were the Ilford Rapid Process Panchromatic and sufficient number of photographs were taken so as to enable a set of bands to come with measurable density. All observations were taken from microphotometer records. The measured intensities were duly corrected for energy distribution ($E_{\lambda} \cdot \lambda$ curve) of the lamp and the varying sensitivity of the photographic plate in different regions of the spectrum.

Results

(1) *Intensities.*

The results of intensity measurements are entered in the following $v'-v''$ (Table I) with 0—0 band as 100. The 0—0 band being very strong in

TABLE I
Intensities and I/ν^4 Values.

$v' \backslash v''$	0	1	2	3	4	5	6	7	$\Sigma I/\nu^4$
0	100 22.57	11.27 3.54	1.26 .74						26.85
1	10.26 1.68	50.23 11.19	12.08 3.72	2.09 0.91					17.50
2		12.45 2.04	28.64 0.32	10.75 3.26	1.37 0.58				12.20
3			5.22 0.85	16.44 3.60	10.15 3.04	1.04 0.43			7.92
4					10.82 2.35	8.15 2.42	1.01 0.41		5.18
5							7.26 2.13	0.87 0.35	2.48

comparison to 0, 1 or 0, 2, a number of intermediate exposures had to be made to express it on the relative scale.

The intensity of a band connected with a given pair of vibrational levels $v'-v''$ is proportional to ν^4 , to the number of molecules in the initial level and to the probability of the transition from the initial to the final level. If the distribution in the initial level corresponds to thermal equilibrium

at an absolute temperature T , the number of molecules with the vibrational energy $E_{v'}$ is proportional to the Boltzmann factor $e^{-\frac{E_{v'}}{kT}}$ and the intensity of a band can be written down as $I = C \cdot \nu^4 p_{v'v''} \cdot e^{-\frac{E_{v'}}{kT}}$ where p = transition probability, C = constant, the other symbols having their usual significance. Consequently I/ν^4 values are calculated separately for each band and these are put below the intensity values in the above table. The sum $\Sigma I/\nu^4$ for each initial level is put in the last column of the table and these numbers represent values proportional to the statistical weight of the level.

(2) Effective Temperature of the Arc

The data $\Sigma I/\nu^4$ from Table I have been utilized to calculate 'effective' temperature of the source. In the case of $\text{CN } ^2\Sigma \rightarrow ^2\Sigma$ system, the following equation holds for the vibrational energy in the upper state:

$$2164 \cdot 15 (v' + \frac{1}{2}) - 20 \cdot 25 (v' + \frac{1}{2})^2 = 1 \cdot 6083 T \log_{10} \frac{N_0}{N_{v' + \frac{1}{2}}}$$

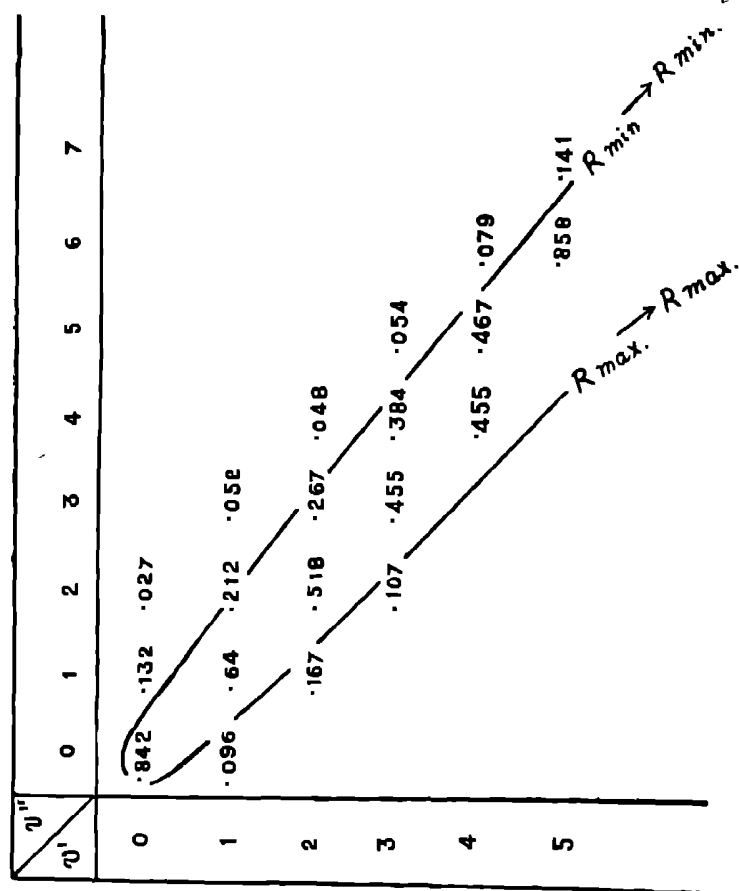


FIG. 1. Transition Probabilities.

The values of N , the number of molecules are taken proportional to $\Sigma I/\nu^4$ in each initial level. By plotting $\log_{10} \frac{N_0}{N_{v'+\frac{1}{2}}}$ against the vibrational energy it is possible to get the value of T the absolute temperature from the slope of the linear relation and this has been found in our case to be $7210 \pm 500K$.

(3) *Transition Probabilities*

Fig. 1 above has been constructed giving numbers proportional to vibrational transition probabilities. They have been calculated according to procedure adopted in a previous paper from I/ν^4 values of Table I. They represent only relative values. The Condon parabola of maximum transitions has been shown as a curve passing through preferred vibrational levels. Its agreement with theory can be judged from the following Table II which gives comparative values.

TABLE II
Transition Probabilities
Comparative Values

Experimental	Morse	Rydberg
$r_{\max} \rightarrow r_{\max}$		
4, 4	4, 3 and 1, 4	4, 4
3, 2 and 3, 3	3, 2	3, 2 and 3, 3
2, 2 and 2, 1	2, 1	2, 2 and 2, 1
1, 1	1, 0 and 1, 1	1, 0 and 1, 1
0, 0	—	0, 0
$r_{\min} \rightarrow r_{\min}$		
5, 6 and 5, 7	5, 7	5, 7
4, 5	4, 6	4, 6
3, 4	3, 5	3, 5
2, 3	2, 4	2, 4
1, 2	1, 2	1, 2
0, 1	0, 1	0, 1 and 0, 0

Column 1 of the Table gives experimental transitions, while columns 2 and 3 give the transitions as derived theoretically by graphical method from Morse and Rydberg functions. The potential energy curves drawn to scale according to these are shown in Figs 2 and 3

(4) Behaviour in Sequences

It has been shown by Ornstein and Brinkman¹ that in the sequences of this system, there is a linear relation between $\log I/\nu^4$ of a band and the vibrational energy $F_{v'}$. This means that the vibrational transition probabilities in each sequence are proportional to $e^{-\alpha E_{v'}}$ after a certain value of v' , α being a constant. The linearity of this relation in some sequences has been verified by the author in a previous paper.⁶ Calculation of the value of α gives in the case of $v'-v''=0$ sequence $\alpha = +1.15 \times 10^{-4}$ and that

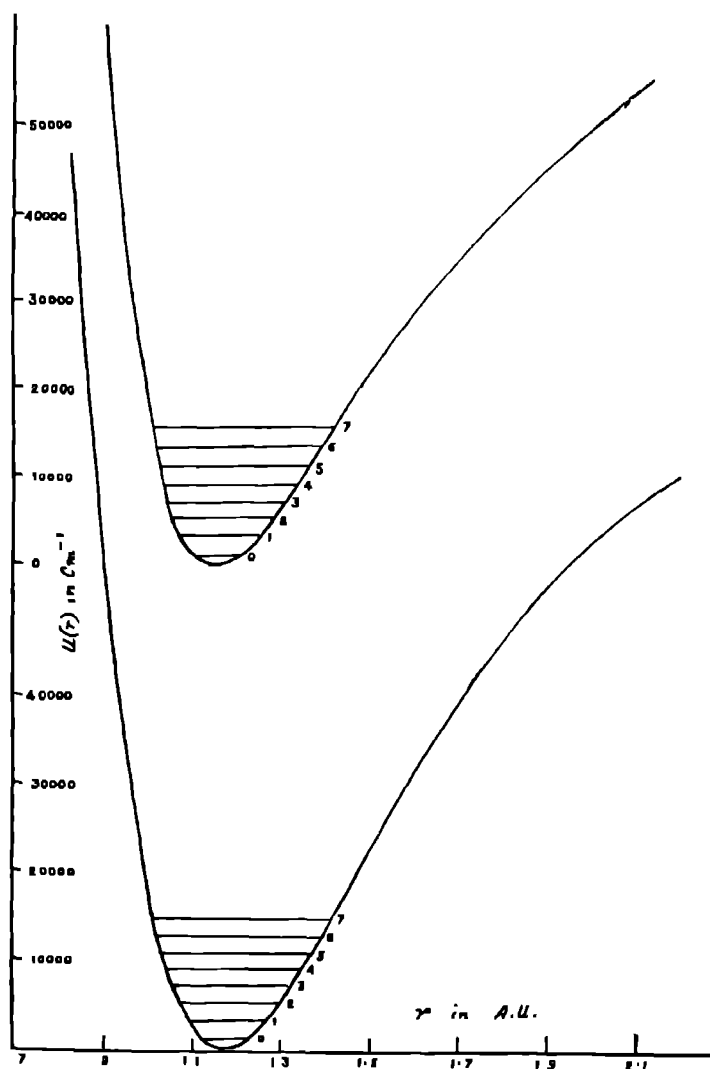


FIG. 2. Morse Potential Energy Curves for Violet CN System.

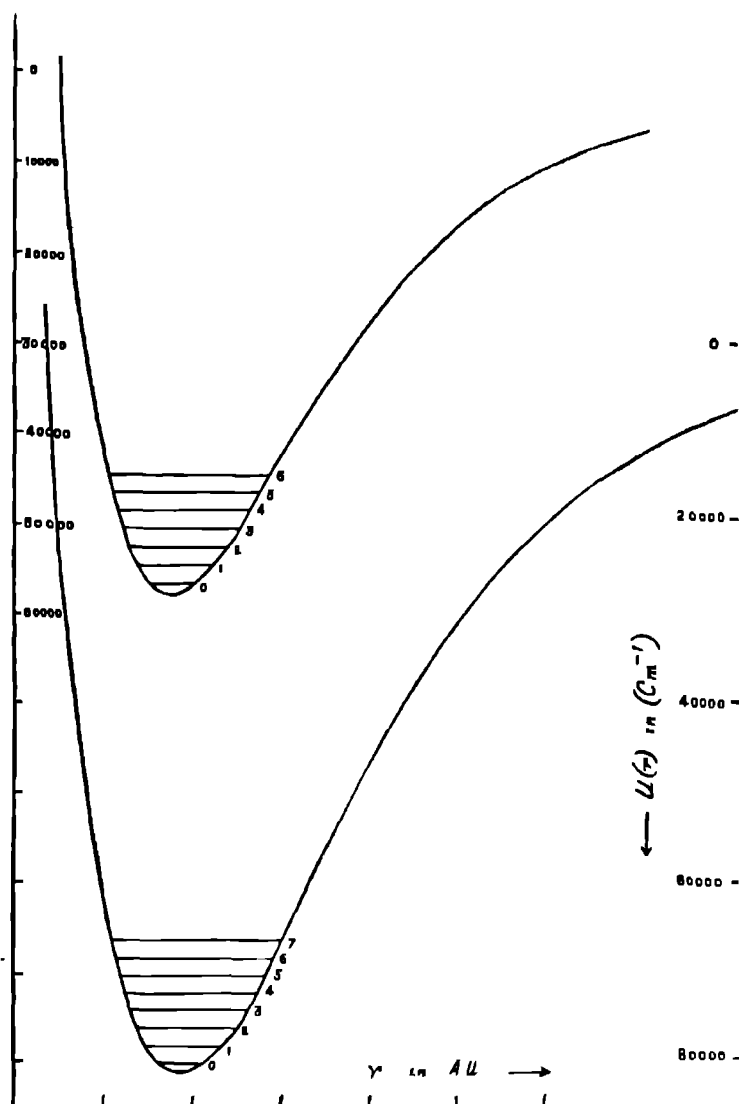


FIG. 3. Rydberg $U(r)$ Curves for Red CN System.

in the case of $v'-v'' = -1$ it equals -1.38×10^{-4} on a relative scale. For $v'-v'' = +1$ and -2 sequences the value of α is not very well defined, but it is near about -1.317×10^{-4} in the case of the latter. In general, it appears that $\alpha > 0$ in sequences $v'-v'' = 0$ and $+1$ and $\alpha < 0$ in sequences $v'-v'' = -1$ and -2 as indicated by Ornstein and Brinkman¹

Conclusions

In deriving the effective temperature of the radiating source, a linear relation was found between the 'weights' of the various initial levels and the vibrational energy. This shows that there is thermal equilibrium of molecules at the temperature of the source and a vibration temperature does exist in this case, but its value is rather too high for the source used. However, according to Ornstein and Brinkman,¹ temperatures between

5,000°K. and 7,000°K. exist in the carbon arc depending on the current and length of the arc as determined by spectroscopic methods. They have found in the case of CN bands a vibration temperature 5,870° K. for a current of 1.7 amp. in the carbon arc. Considering this, the temperature 7,210°K. ± 500 in our case (for current strength 3 amps.) is not improbable, especially in view of the probable sources of error due to unknown causes in this type of work. If in different zones of the arc different temperatures exist, it is quite likely that two band systems arising in the same arc source but giving two different effective temperatures for that source, are excited in different zones. This aspect of the problem requires elucidation and work in this direction is in progress.

There is not much to differentiate between the results of maximum transition probabilities as derived from Morse and Rydberg potential energy functions. Both the curves agree well within the observed limits of the vibrational levels of the system. The Condon parabola derived from both is practically the same and there is satisfactory agreement of the experimental curve with this parabola as can be seen from Fig 1 and Table II. The narrowness of the parabola is to be expected for a molecule of this type where $r'_e < r''_e$.

The theoretical aspect of the subject of spectral intensities in band systems has been treated by Hutchisson⁵ on the basis of quantum mechanics. Hutchisson considers that his formula for calculating the intensity of vibrational levels is applicable to symmetric molecules only, but Dunham⁷ shows that it is of general applicability. Hence in CN which is a non-symmetric molecule, it should be possible by Hutchisson's formula to calculate theoretical intensities and to see their agreement with experiment. It is intended to investigate this in a later paper.

The experimental part in connection with this problem was carried out at the University of London King's College and all the later work was done at the Royal Institute of Science, Bombay. The author is much indebted to Dr. R. C. Johnson for his interest in the work and to Prof. A. Fowler of the Royal College of Science, London, for allowing the use of his microphotometer.

Summary.

Quantitative estimation of vibrational intensities in $^2\Sigma \rightarrow ^2\Sigma$ system of CN has been made by the method of heterochromatic spectral photometry.

The results have been utilized to examine some aspects of Condon's theory and effective temperature derived on the assumption of the thermal distribution of molecules in vibrational levels.

Some features of intensities in sequences are discussed.

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THE ABSORPTION SPECTRA OF SOME AROMATIC COMPOUNDS.

Part I.—Hydrocarbons.

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(Communicated by Prof K S Krishnan, D Sc)

1. Introduction

THE absorption spectra of benzene and some of its simple derivatives have been studied in great detail by Henri¹ and his collaborators, and they yield much useful information regarding the optical and other constants of the molecules. For molecules containing more than one benzene ring, the analysis of the spectrum is naturally more difficult. Some of the molecular constants, however, are easily obtained, as for example, the electronic frequencies of the molecule, and its vibration frequencies in the normal and in the excited states. It would be of interest to follow the progressive variation of these constants and of the general characteristics of the absorption bands, with the addition of extra benzene rings, both of the condensed and uncondensed types, in different positions, and to interpret these variations in relation to the structure of these molecules. The present paper concerns itself with such a study. Several aromatic hydrocarbons are studied for their absorption spectra in the vapour state, and among them are (1) naphthalene, anthracene, and naphthacene, with linear condensed benzene rings; (2) phenanthrene, chrysene, and dibenzanthracene, with side condensed rings; (3) pyrene and perylene, with close-packed rings, (4) acenaphthene, fluorene and fluoranthene, with incomplete rings; (5) diphenyl, terphenyl, diphenylmethane, dibenzyl, triphenylmethane and triphenylbenzene, with uncondensed benzene rings, and (6) durene and hexamethylbenzene. The results are discussed in relation to the structure of the molecules and their characteristic electronic and vibrational frequencies.

Since the absorption spectra of the molecules are known to be considerably influenced by the state of aggregation of the molecules, we have also studied the absorption spectra of these substances in the state of solution in different

¹ Henri, *Jour. Physique*, 1922, 3, 181, Orndorff, Gibbs, McNulty and Shapiro, *Jour. Am. Chem. Soc.*, 1928, 50, 831

solvents, and, occasionally in the molten and in the solid states as well. The positions of the absorption bands of a substance in the different physical states are compared.

2 Experimental.

The absorption measurements for the vapours extended in general, from 7000 Å to 2300 Å, and were made with a Hilger quartz E_2 spectrograph. Where the absorption bands were very sharp, Hilger F_1 spectrograph, with a much higher dispersion, was used. Iron arc was used as the standard for the wave-length measurements.

The source of continuous spectrum used for the absorption measurements in the ultra-violet was a specially designed water-cooled hydrogen discharge tube described in an earlier publication by the author,² giving an intense spectrum upto about 2100 Å. For the visible and the near ultra-violet regions a Zeiss tungsten linear filament lamp, fitted with a quartz window, was found to be a more suitable source.

The substances were in general obtained from standard firms,³ and were further purified by crystallisation or sublimation.

The absorption spectra of the solutions were studied in the usual manner with a graduated Baly absorption tube fitted with quartz windows.

For the study of the absorption in the vapour state, the substance was introduced in an absorption tube of pyrex glass, 75 cms long and 2 cms. in diameter, fitted with quartz windows at the ends. It was placed in a suitably devised air oven with a double jacket, where it could be heated and maintained at any desired temperature up to 300° C. (All the substances studied here melt below 250° C.) The temperature of the absorption tube was raised in stages of 10° C, and the absorption spectrum was photographed at each stage. From these absorption spectra, corresponding to gradually increasing vapour pressures, photographed in succession the intensity wave-length curves can be easily traced on an arbitrary scale, just as in the absorption photographs for the solution by the Baly method in which the thickness of the column of solution is gradually increased. The positions of the maxima and the minima of absorption are located in this manner more precisely than from single photographs of the absorption.

The absorption and fluorescence spectra of single crystals of many of these hydrocarbons have been studied by us in detail, particularly in relation to the influence of the direction of vibration of the incident light with reference to the crystal axes on the positions and the intensities of the bands. A

² *Jour. Sci. Instruments*, 1935, 12, 230.

³ The author's thanks are due to Prof. L. F. Fieser of the Harvard University and to Prof. A. Dadiou of the Vienna University for the supply of naphthalene and perylene.

report of this work is being published separately, to which the reader may be referred for a description of the experimental arrangement used for these absorption measurements, and for the details of the results. We may mention here that though the intensities of the various absorption bands show a remarkable dependence on the direction of the light-vector in the crystal, the *positions* of the bands are practically independent of the direction of the vector. The data for the positions of the absorption bands in the solid state quoted in the next section are all taken from this paper.

3 Results

The experimental results are collected together in this section. The different substances are considered separately, and the special characteristics of the bands are described under each. In the tables are entered the wavelengths of the absorption maxima, and the corresponding wave numbers in cm^{-1} . The difference between the wave-numbers of successive bands are entered in the next column. The intensities of the bands are indicated by arbitrary numbers.

The absorption data for the substance in solution in alcohol, and for the substance in the solid state, are also given for comparison with the vapour data. On comparing the absorption spectra for the solid, liquid and the solution with that of vapour, we find that the positions of the bands are widely different; even for the solutions they are different for different solvents. A closer comparison of the spectra in the different physical states, however, shows that except for a bodily shift of the absorption spectra towards the longer-wave-length side as we go from the vapour to the solution, and further in the same direction as we go from solution to molten liquid and still further when we pass to the solid, and a progressive change in the diffuseness of the bands, the relative positions of different components of the bands system are more or less the same for the different physical states. There is thus an approximate one to one correspondence between the prominent absorption bands in the different states; the corresponding bands in the different states are also easy to identify. In the following tables the data for the corresponding bands in the different physical states are entered in the same *row*, so as to facilitate comparison.

The actual absorption spectrograms are also reproduced, from which the general nature of the absorption bands and their other characteristics will be clear.

Among the substances studied here naphthalene vapour has been already studied in great detail by Henri and Laszlo.⁴ Some preliminary

⁴ Henri and Laszlo, *Proc. Roy. Soc., A*, 1926, 105, 355; Laszlo, *Zeits. Phys. Chem.*, 1925, 118, 369.

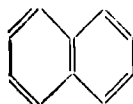
absorption measurements are available for the anthracene vapour,⁵ and for solid anthracene and phenanthrene at low temperatures.⁶ In the state of solution most of these substances have previously been studied, by Baly,⁷ Clar,⁸ Dadiou⁹ and others. The solution data given in the tables are those obtained by us, and they agree well with those given by these earlier investigators. Alcohol was the usual solvent in our measurements.

In general the absorption spectrum consists of a large number of prominent bands more or less equally spaced; the spacing interval is about 1300 to 1400 cm^{-1} . These bands are accompanied by feeble satellites usually one each, on the shorter-wave-length side, separated from the main band by about 400 cm^{-1} . They do not generally exhibit any rotational fine structure, naphthalene and acenaphthene are striking exceptions.

Accompanying this banded absorption there is also a strong background of continuous absorption, which consists of two distinct regions separated by a region of transmission. The first absorption region, usually in the near ultra-violet, begins more or less abruptly, and reaches a feeble maximum. Beyond it is a region of relative transparency, and further beyond begins the second region of absorption, which is much stronger than the first. For some of the substances there is also a second region of feeble transmission in the ultra-violet. The bands in the first region stand out from the continuous background much more prominently than those in the second region; indeed in the second region two or three bands only can be observed, near the long-wave-length end of the region.

We now proceed to the detailed report of the results.

1. *Naphthalene*



See Figs. 1 (a) and (b), Plate V. Many of the bands in the long-wave-length region exhibit fine-structure and they are indicated by an asterisk; a double asterisk indicates that the fine-structure is very prominent. There is a region of transmission from 2600 Å to 2250 Å, beyond which there is again absorption; the bands in the latter region are broad and diffuse. The bands in the solution and solid state do not show any fine-structure.

⁵ Capper and Marsh, *Jour. Chem. Soc.*, 1926, 724

⁶ Obreimow and Prichotjko, *Phys. Zeits. Sow. Union*, 1932, 1, 203.

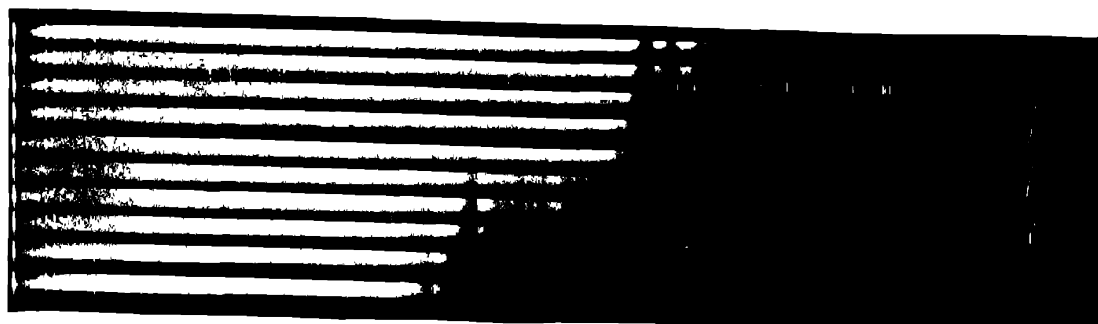
⁷ *Jour. Chem. Soc.*, 1908, 93, 1902

⁸ Several papers in *Berichte*, 1931–1933

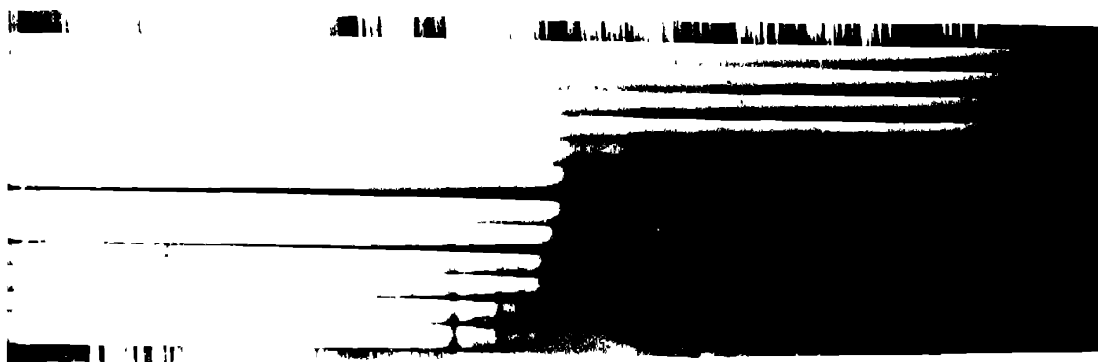
⁹ *Zeits. Phys. Chem.*, 1933, 135, 347.

TABLE 1 *Absorption spectrum of naphthalene.*

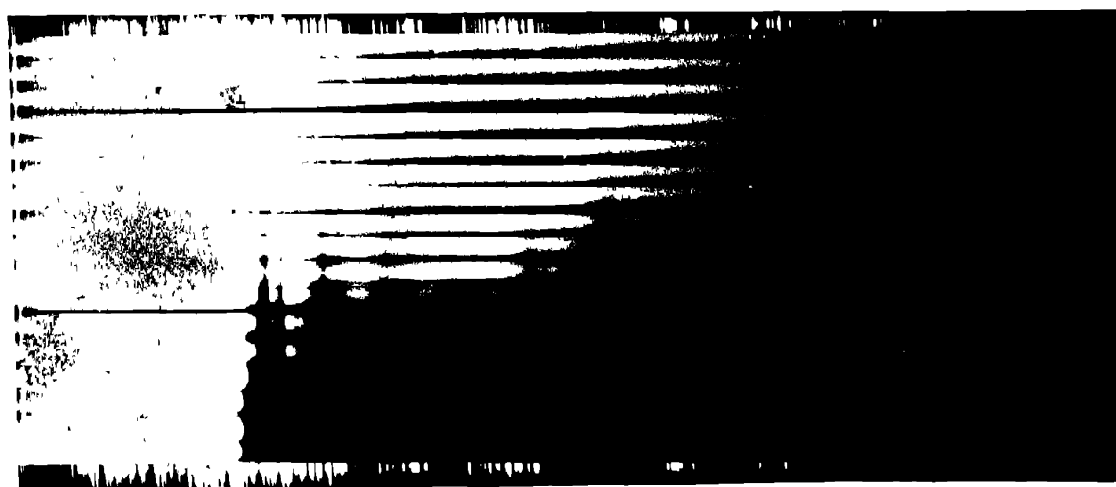
Vapour			Solution			Solid		
λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
**	3190	31320				3270	30580	
		460						450
*	3145	31780	3190	31320		3220	31030	
		240			460			410
**	3120	32020	3145	31780		3180	31440	
		370			470			500
**	3085	32390	3100	32250		3130	31940	
		340			↑			400
**	3055	32730			420	3090	32340	
		200 ↑			↓			470
*	3035	32930	3060	32670		3045	32810	
		220 ↓			320			
**	3015	33150	3030	32990				
		290 ↑			220			
*	2990	33440	3010	33210				
		200 ↓						
**	2975	33610			340			
		420						
*	2935	34060	2980	33550				
		290			450			
*	2910	34350	2940	34000				
		400			590			
*	2875	34750	2890	34590				
		350			360			
	2850	35100	2860	34950				
		310			370			
	2820	35410	2830	35320				
		420			460			
**	2790	35830	2795	35780				
		450			310			
*	2755	36280	2770	36090				
		470			460			
*	2720	36750	2735	36550				
		410						
*	2690	37160						
		490						
*	2655	37650	2670	37440				
		450						
*	2625	38100						
		570						
	2585	38670						
		450						
	2555	39120	2590	38590				
		480						
	2525	39600						
		470						
	2495	40070						



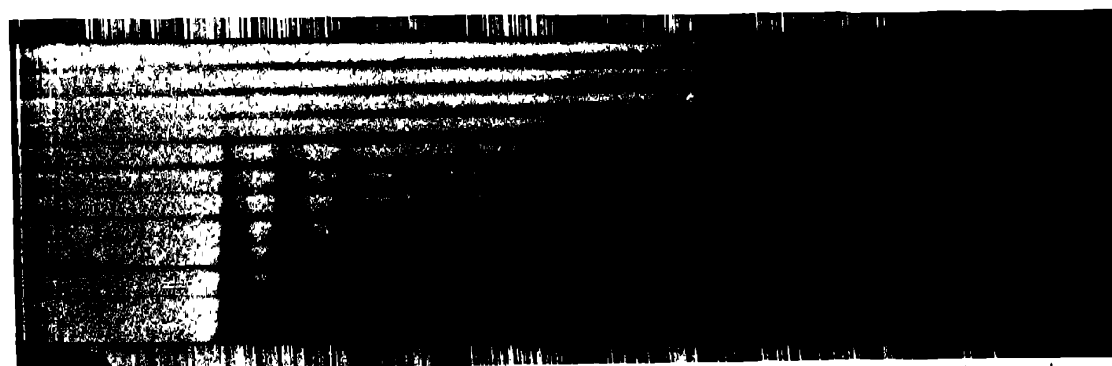
1 (a)



1 (b)



2 (a)



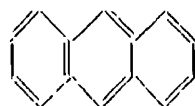
2 (b)

—λ
—4400 —3650 —3300 —3100 —2850 —2630 —2500 —2400

FIG. 1. Naphthalene (a) Vapour, (b) Solution

FIG. 2. Anthracene (a) Vapour, (b) Solution.

2. Anthracene.



Figs. 2 (a) and (b), Plate V In the first region of absorption, which extends from about 3700 Å to 3100 Å, the absorption bands appear prominently, the continuous background being very feeble. The bands are spaced at intervals of 1400 to 1350 cm⁻¹, and many of them are accompanied by satellites at intervals of 350 to 400 cm⁻¹.

In solution and in the solid state, most of these satellites disappear, the bands retaining only one satellite each, on the short-wave-length side at 400 cm⁻¹.

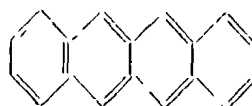
Near about 3100 Å is the region of feeble transmission, and as will be seen from the photographs, there is an indication of another such region much less transparent, at about 2600 Å.

TABLE 2 Absorption spectrum of anthracene

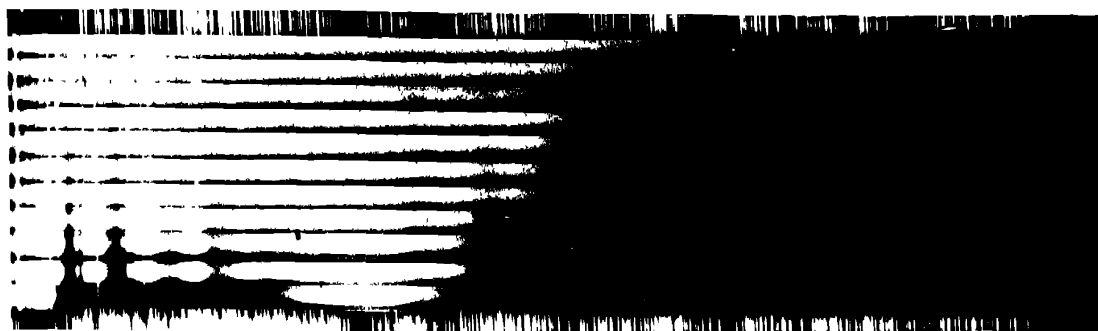
Int.	Vapour			Solution			Solid		
	λ	ν	Δν	λ	ν	Δν	λ	ν	Δν
1	3680	27170					4000	24990	
			370						550
5	3730	27540		3750	26660		3915	25540	
			390 ↑			430 ↑			460 ↑
3	3580	27930		3690	27090		3845	26000	
			430 ↑						
2	3525	28360	1480			1460			1480
			240 ↓						
1	3495	28600							
			420 ↓						
5	3445	29020		3555	28120		3700	27020	
			380 ↑			400 ↑			440 ↑
3	3400	29400		3505	28520		3640	27460	
			400 ↑			1460			1460
2	3355	29800	1460						
			↓						
4	3280	30480		3380	29580		3510	28480	
			370 ↑			400 ↑			370 ↑
2	3240	30850	1410	3335	29980	1420	3465	28850	1450
			↓			↓			↓
3	3135	31890		3225	31000		3340	29930	
			410 ↑			440 ↑			
1	3095	32300	1440	3180	31440	1460			1410
			↓			↓			↓
5	3000	33330		3080	32460		3190	31340	

TABLE 2—(Contd.)

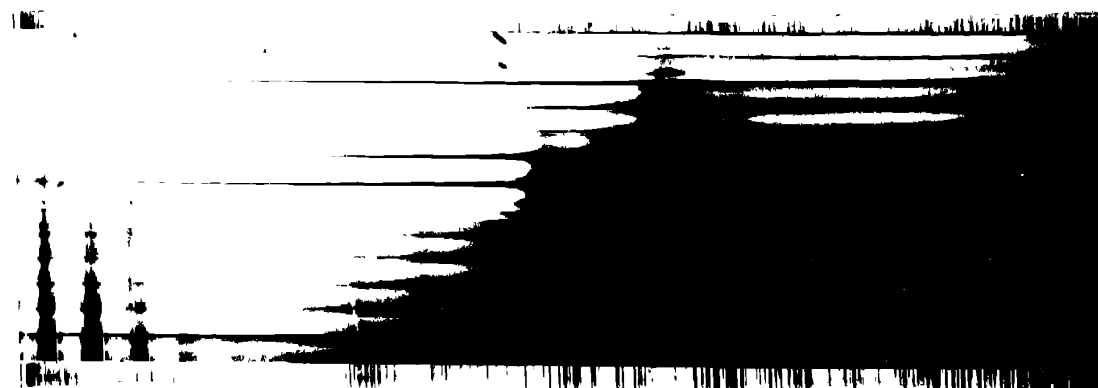
Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
1	2960	33770	440 ↑ 1500			1490 ↑ ↓			
7	2870	34830	↓	2915	33950	↓			
4	2840	35200	370 ↑			↑			
2	2790	35830	1390 ↓			1410 ↓			
7	2760	36220	390 ↓	2825	35390	↓			
4	2730	36620	400 ↑			↑			
2	2700	37030	410 ↑ 1500			1430 ↑ ↓			
2	2680	37300	270 ↓			↓			
7	2650	37720	420 ↓	2715	36820	↓			
4	2620	38160	440 ↑ 1410			1410 ↑ ↓			
8	2555	39130	↓	2615	38230	↓			
10	2460	40640	1510	2520	39670	1440			
10	2380	42080	1440						
10	2300	43460	1380						

3 *Naphthalene*

The absorption spectrum of this substance bears a striking resemblance to that of anthracene, the main bands being spaced at intervals of 1350 to 1400 cm^{-1} , with satellites at intervals of 400 cm^{-1} . The continuous spectrum in region I is even less feeble than in anthracene, and the bands appear therefore more prominently than in anthracene. See Figs 3 (a), (b), (c) and (d), Plate VI.



3

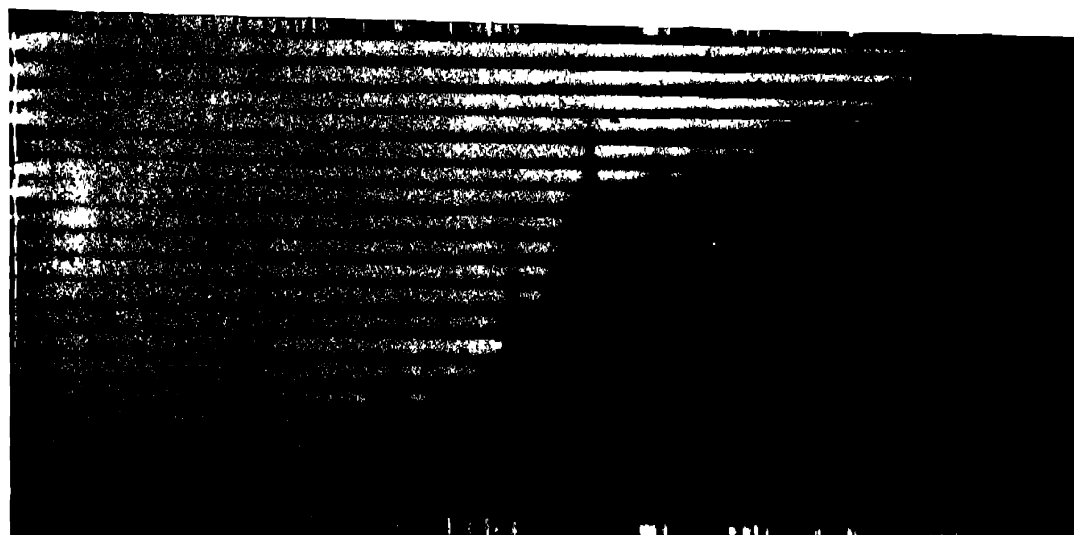


3

3 (c)



3 (c)



4 (a)

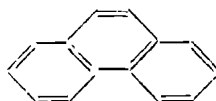
FIG. 3 Naphthalene (a) Vapour, (b) Solution.
(visible region) (c) Vapour, (d) Solution.

FIG. 4. Phenanthrene. (a) Vapour

TABLE 3. Absorption spectrum of naphthacene.

Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
6	4500	22220		4680	21360		4850	20610	
4	4415	22640	420 ↑	4595	21750	390 ↑			1460 ↑
2	4335	23060	420 1410 ↓			1410 ↓			1460 ↓
6	4230	23630		4390	22770		4530	22070	
4	4160	24030	400 ↑	4310	23190	420 ↑			1450 ↑
1	4090	24440	410 1390 ↓			1410 ↓			1450 ↓
5	3995	25020		4135	24180		4250	23520	
3	3930	25440	420 ↑	4060	24620	440 ↑			
			1390 ↓			1390 ↓			
5	3785	26410		3910	25570				
			1440			1410			
4	3590	27850	1380	3705	26980	1380			
3	3420	29230		3525	28360				
6	3195	31290		3335	29980				
			1380			1410			
8	3060	32670	1330	3185	31390	1280			
10	2940	34000	1320	3060	32670	1330			
10	2830	35320	1300	2940	34000	1260			
10	2730	36620	1320	2835	35260	1290			
9	2635	37940	1260	2735	36550	1310			
8	2550	39200		2640	37860				

4 Phenanthrene.

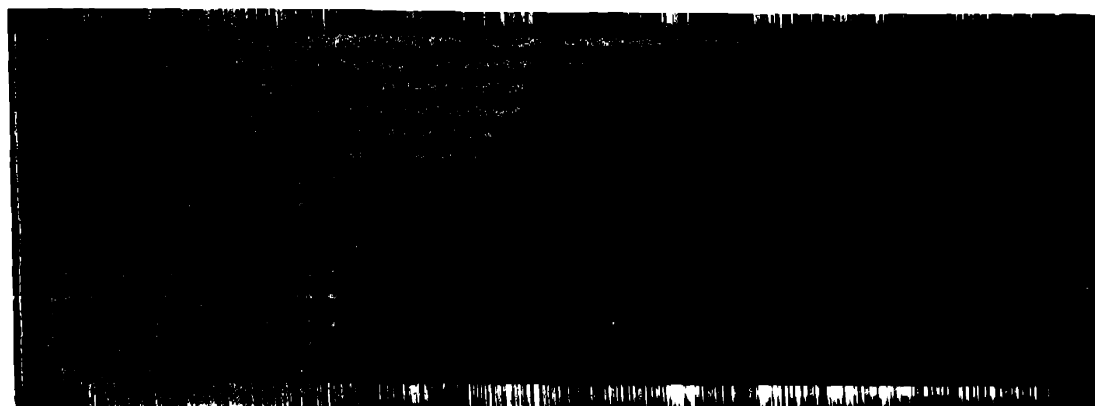


Figs. 4 (a) and (b), Plates VI and VII. The compound contains usually, as was pointed out by Capper and Marsh, anthracene as an impurity, and has to be specially freed from the latter.

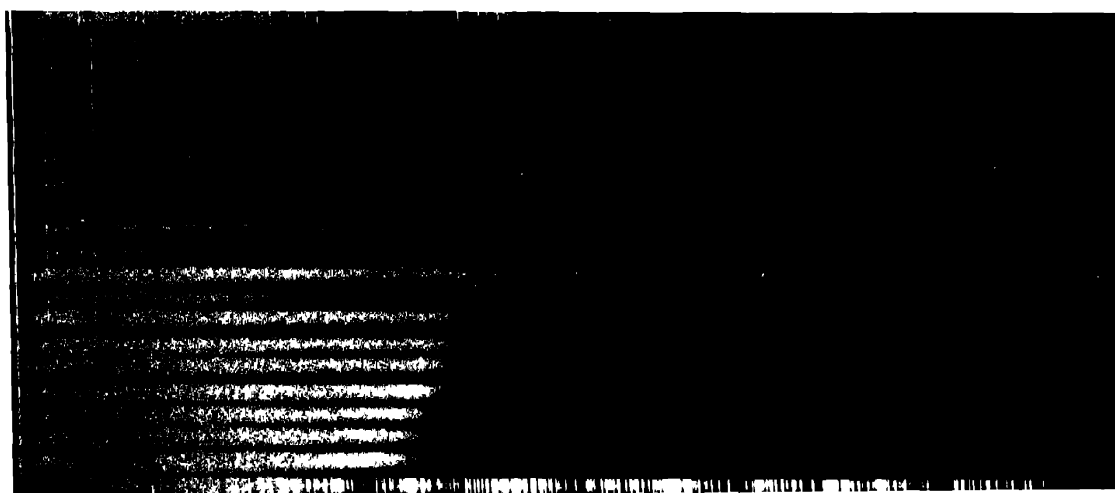
The general nature of both the continuous and the banded absorptions is very different from that of anthracene or naphthacene. The progression of the intensities of the absorption bands does not show the correspondence with that of the continuous absorption accompanying the bands, that is observed in anthracene or naphthacene

TABLE 4. *Absorption spectrum of phenanthrene*

Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
3	3630	27540		3750	26660		3830	26100	
2	3585	27890	350 \uparrow	3695	27050	390 \uparrow	2765	26550	450 \uparrow
			1440 \downarrow			1460 \downarrow		400 \downarrow	1440 \downarrow
3	3450	28980		3555	28120		3710	26950	590 \downarrow
			730 \uparrow			730 \uparrow			
3	3365	29710	1500 \downarrow	3165	28850	1460 \downarrow	3630	27540	780 \uparrow
			770 \downarrow			730 \downarrow			
3	3280	30480		3380	29580		3530	28320	1480 \downarrow
			660 \uparrow			710 \uparrow		700 \downarrow	
3	3210	31140	1410 \downarrow	3300	30290	1420 \downarrow	3145	29020	730 \uparrow
			750 \downarrow			710 \downarrow			
3	3135	31890		3225	31000		3360	29750	1410 \downarrow
			730 \uparrow			790 \uparrow		680 \downarrow	
3	3065	32620	1440 \downarrow	3145	31790	1460 \downarrow	3285	30430	760 \uparrow
			710 \downarrow			670 \downarrow			
3	3000	33330		3080	32460		3205	31190	1460 \downarrow
			730 \uparrow			750 \downarrow		700 \downarrow	
7	2935	34060	1440 \downarrow	3010	33210		3135	31890	780 \downarrow
			710 \downarrow			910 \downarrow			
4	2875	34770		2930	34120		3060	32670	
			490 \downarrow			470 \uparrow			
10	2835	35260		2890	34590				
			320 \uparrow			430 \uparrow			
8	2810	35580		2855	35020				
			380 \uparrow						
8	2780	35960	1430 \downarrow			1460 \downarrow			
			330 \downarrow						
8	2755	36290							
			400 \downarrow						
9	2725	36690		2810	35580				
			750 \uparrow						
9	2670	37440	1470 \downarrow			1450 \downarrow			
			720 \downarrow						
7	2620	38160		2700	37030				
			1430 \downarrow			1420 \downarrow			
8	2525	39590		2600	38450				
			1450 \downarrow			1460 \downarrow			
10	2435	41040		2505	39910				
			1410 \downarrow			1480 \downarrow			
10	2355	42450		2415	41390				



4 (b)



5 (a)



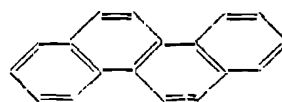
5 (b)



6

FIG. 4.—Phenanthrene . (b) Solution.

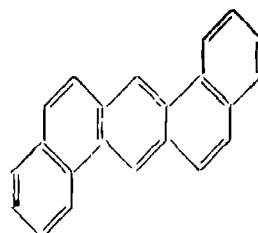
5. Chrysene (1·2 Benzophenanthrene).



The spectrum resembles that of phenanthrene. Figs. 5 (a) and (b), Plate VII.

TABLE 5. Absorption spectrum of chrysene.

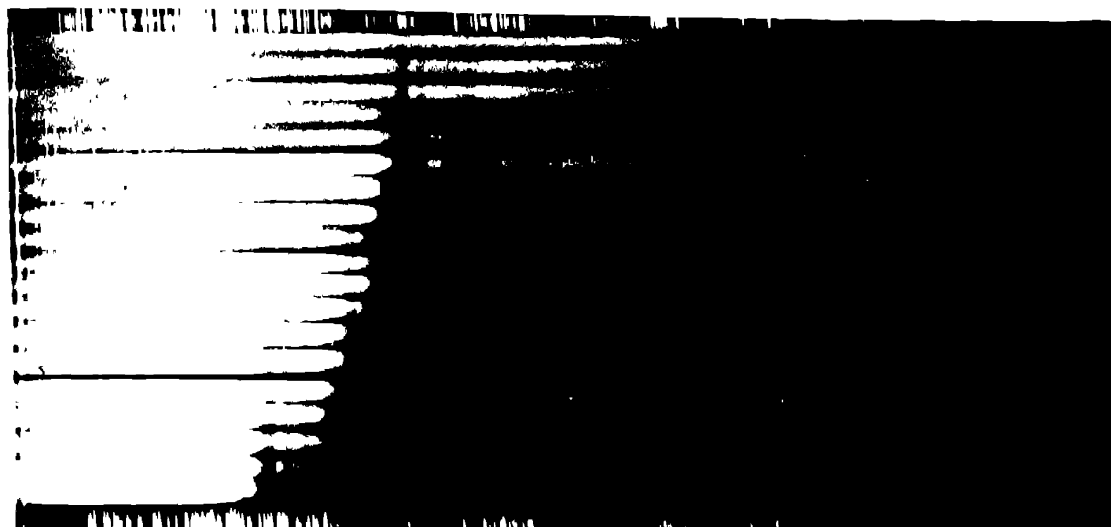
Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
5	3605	27730		3745	26690		3920	25510	
			750 \uparrow			770 \uparrow			450
4	3510	28480	1420	3640	27460	1510	3850	25960	
			670 \downarrow			740 \downarrow			460
2	3130	29150		3545	28200		3785	26420	
			780 \uparrow			730 \uparrow			460
3	3340	29930	1520	3455	28930	1500	3720	26880	
			740 \downarrow			770 \downarrow			440
1	3260	30670		3365	29700		3660	27320	
			770 \uparrow			\uparrow			440
1	3180	31440	1580			1540	3600	27760	
			810 \downarrow			\downarrow			410
3	3100	32250		3200	31240		3550	28170	
			370 \uparrow			\uparrow			480
1	3065	32620	1300			1320	3490	28650	
			\downarrow			\downarrow			500
3	2980	33550		3070	32560		3430	29150	
			340 \uparrow			\uparrow			390
1	2950	33890	1300			1270	3385	29540	
			\downarrow			\downarrow			
3	2870	34850		2955	33830				
			350 \uparrow			\uparrow			
0	2840	35200	1300			1310			
			\downarrow			\downarrow			
6	2765	36150		2845	35140				
			1430			1080			
10	2660	37580		2760	36220				
			720 \uparrow			\uparrow			
5	2610	38300	370			1530			
			\uparrow			\downarrow			
4	2585	38670	1470						
			380 \downarrow						
9	2560	39050		2580	38750				
			1420			1400			
8	2470	40470		2490	40150				
			1450						
7	2385	41920							

6. 1. 2. 5. 6. *Dibenzanthracene*

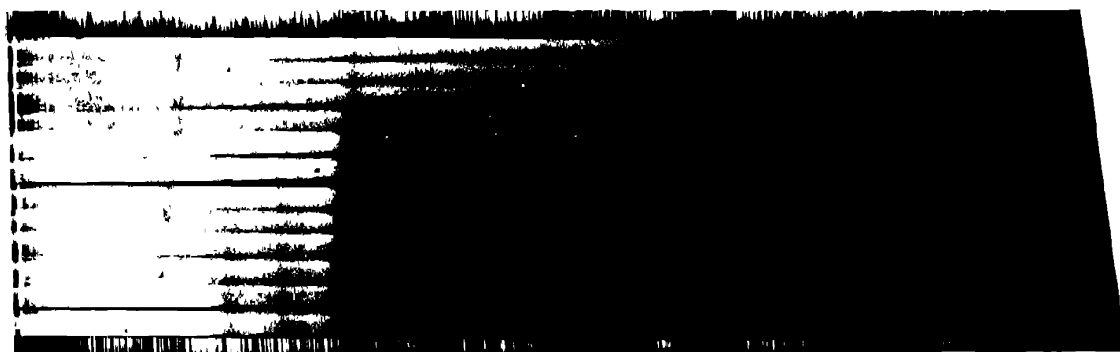
The vapour spectrum was not studied. The substance was, however, studied in solution and in the solid state. See Fig 6, Plate VII

TABLE 6 *Absorption spectrum of dibenzanthracene.*

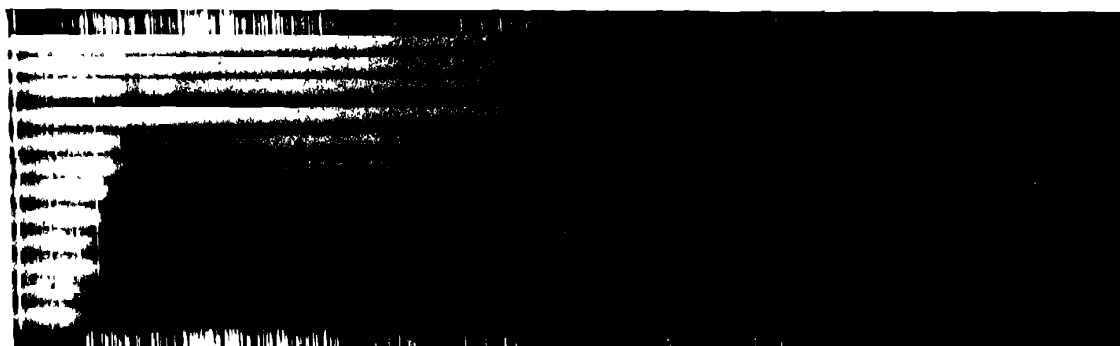
Int.	Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
				4685	21340	
						1380
				4400	22720	
				4040	24740	
						790 \uparrow
2	3970	25190		3915	25530	1460 \downarrow
		700				670
1	3860	25890		3815	26200	
		700				460
2	3760	26590		3750	26660	
		680				730
4	3665	27270		3650	27390	
			1460			1010
2	3480	28730		3520	28400	
		760 \uparrow				
5	3390	29490	1380			1480
		620 \downarrow				
2	3320	30110		3450	28980	
		940 \uparrow				
6	3220	31050	1380			
		440 \downarrow				
6	3175	31490				
		810				
8	3095	32300				
			1360			
9	2970	33660				
			1420			
9	2850	35080				
		880 \uparrow				
10	2780	35960	1540			
			\downarrow			
10	2730	36620				



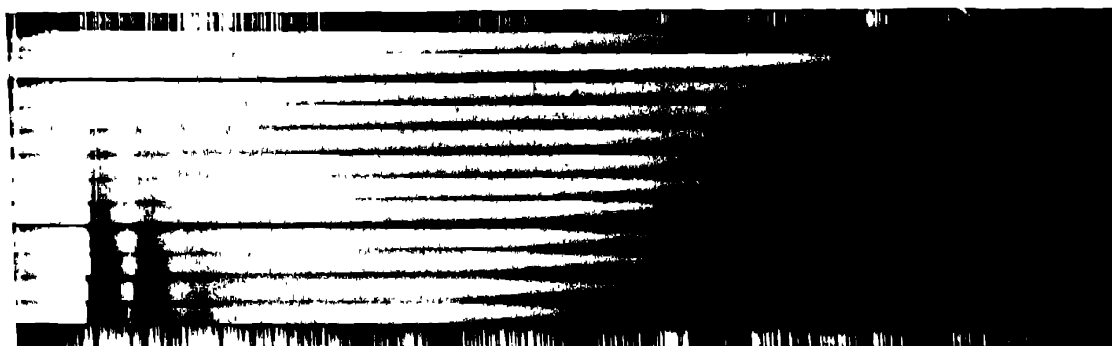
7 (a)



7 (b)



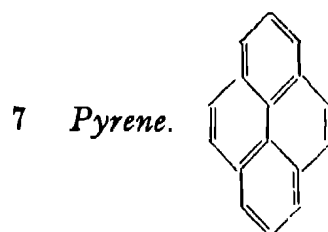
8 (a)



8 (b)

FIG. 7 Pyrene (a) Vapour, (b) Solution.

FIG. 8. Perylene (a) Vapour, (b) Solution



The spectrum resembles more that of the linear ringed compounds like naphthacene and anthracene, than that of phenanthrene or chrysene. It shows however, less details than either anthracene or naphthacene. See Figs. 7 (a) and (b), Plate VIII

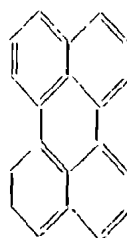
TABLE 7. Absorption spectrum of pyrene.

Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
3	3630	27540		3795	26340		3770	26520	
			540			530			460
2	3560	28080		3720	26870		3705	26980	
			520						450
2	3495	28600					3645	27430	
			590						460
3	3425	29190					3585	27890	
			560						430
2	3360	29750		3500	28560		3530	28320	
			540			500			
2	3300	30290		3440	29060				
			380						
4	3260	30670							
			380						
10	3220	31050		3350	29840				
			390			450			
6	3180	31440		3300	30290				
			400						
4	3140	31840							
			310						
3	3110	32150							
			360						
9	3075	32510		3195	31270				
			370			460			
6	3040	32880		3150	31730				
			330						
4	3010	33210							
			390						
3	2975	33600							
			350						
8	2945	33950		3055	32720				

TABLE 7—(Contd.)

Int.	Vapour			Solution			Solid
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	
5	2920	34240	290 \uparrow			\uparrow	
			350 \uparrow			1400 \uparrow	
3	2890	34590	1440 \downarrow			\downarrow	
7	2825	35390		2930	34120		
			430 \uparrow			\uparrow	
6	2715	36820	480 \uparrow			\uparrow	
2	2680	37300	1330 \downarrow			1390 \downarrow	
			420 \downarrow			\downarrow	
10	2650	37720		2815	35510		
			360 \uparrow			\uparrow	
7	2625	38080	370 \uparrow			\uparrow	
4	2600	38450	1500 \downarrow			1240 \downarrow	
			\downarrow			\downarrow	
7	2550	39200		2720	36750		
			310 \uparrow			\uparrow	
4	2530	39510	1410 \downarrow			1480 \downarrow	
			\downarrow			\downarrow	
5	2460	40640		2615	38230		
			1450 \downarrow			1440 \downarrow	
3	2375	42090		2520	39670		
			1460 \downarrow			1470 \downarrow	
6	2295	43550		2430	41140		

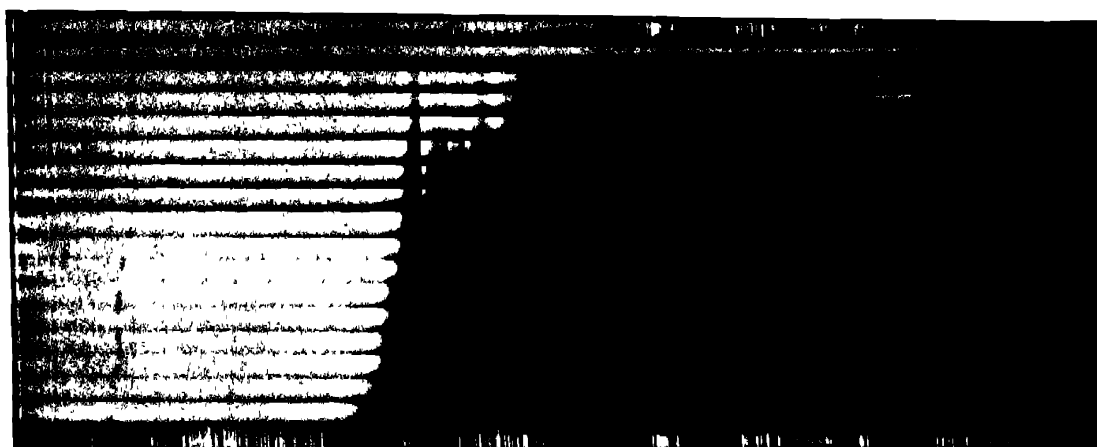
8 Perylene.



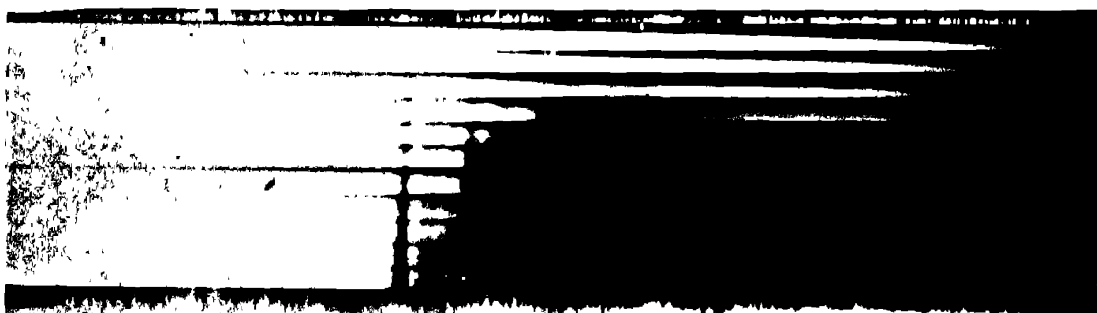
The region of transmission is conspicuous. The spectrum shows very few details, even less than that of pyrene. In addition to the general strong absorption in region II, there seems to be a feeble continuous spectrum, *which starts abruptly* at about 2800 Å, which shows also a feeble banded structure. See Figs. 8 (a), (b), (c) and (d), Plates VIII and IX.



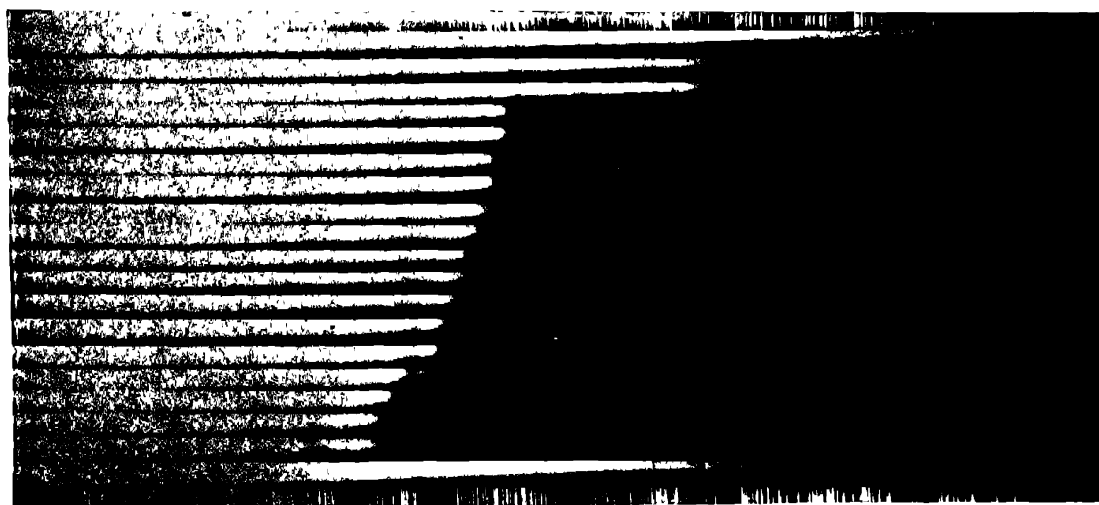
8 (



9 (



9 (



10

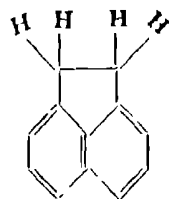
FIG. 8. Perylene (visible region) (a) Vapour, (b) Solution.

FIG. 9. Acenaphthene (a) Vapour, (b) Solution.

FIG. 10. Fluorene: (a) Vapour

TABLE 8.
Absorption spectrum of perylene.

Int.	Vapour			Solution		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
2	4245	23550				
		480				
6	4160	24030		4250	23520	
		500			480	
4	4075	24530	\uparrow	4165	24000	\uparrow
		490	1470			1440
3	3995	25020	\downarrow			\downarrow
		480				
5	3920	25500		4005	24960	
		460			510	
4	3850	25960	\uparrow	3925	25470	\uparrow
		490	1410			1450
3	3780	26450	\downarrow			\downarrow
		460				
5	3715	26910		3785	26410	
		480			500	
4	3650	27390	\uparrow	3715	26910	\uparrow
		510	1490			1440
3	3585	27900	\downarrow			\downarrow
		500				
4	3520	28400		3590	27850	
			1440			1470
3	3350	29840	1450	3410	29320	1440
1	3195	31290	1490	3250	30760	
1	3050	32780	1400			
0	2925	34180	1460			
0	2805	35640	1450			
2	2695	37090	1430	2850	35080	1470
3	2595	38520	1470	2735	36550	1460
4	2500	39990	1400	2630	38010	1430
3	2415	41390	1510	2535	39440	
3	2330	42900				

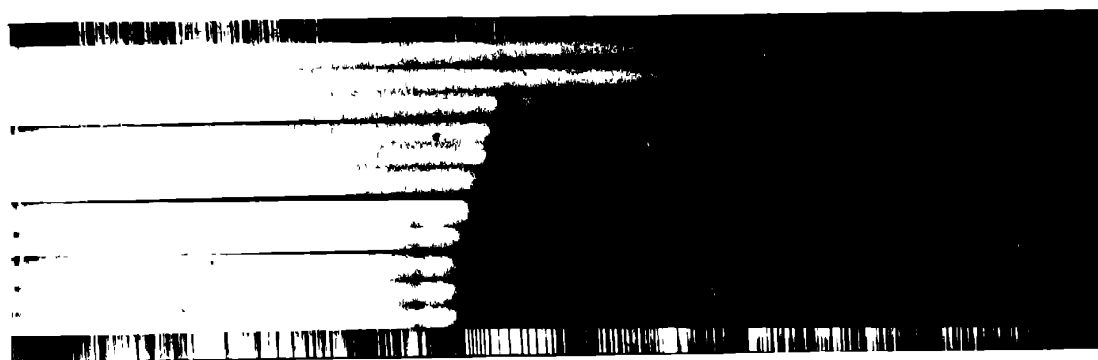
9. *Acenaphthene*.

The most striking feature of the spectrum of this substance is the sharp edge of the bands on the short-wave-length side

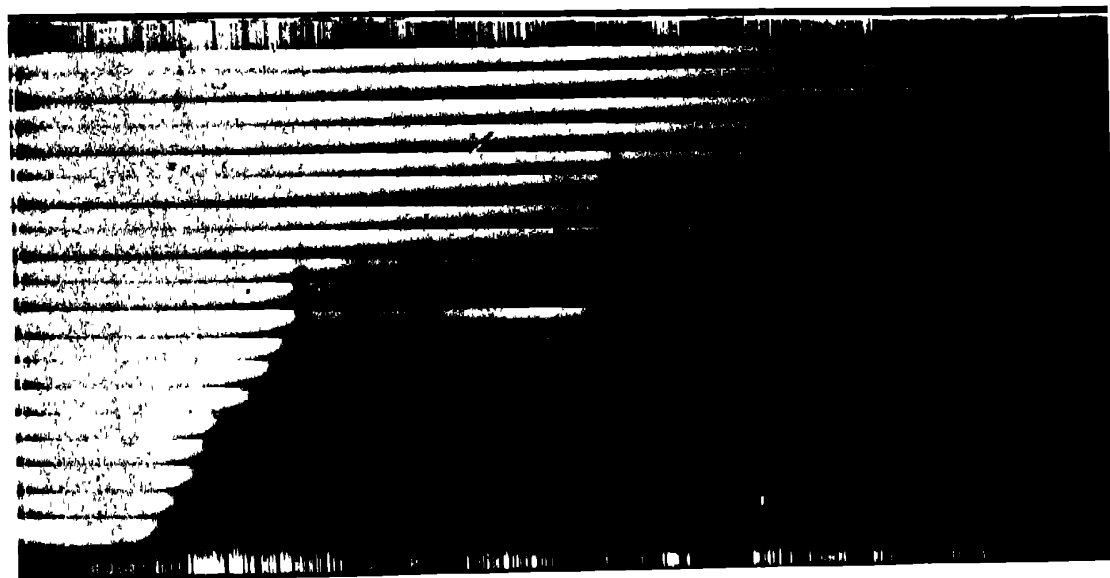
There is a very feeble transmission at about 2450 \AA . The spectrum closely resembles that of naphthalene. See Figs 9 (a) and (b), Plate IX.

TABLE 9.
Absorption spectrum of acenaphthene

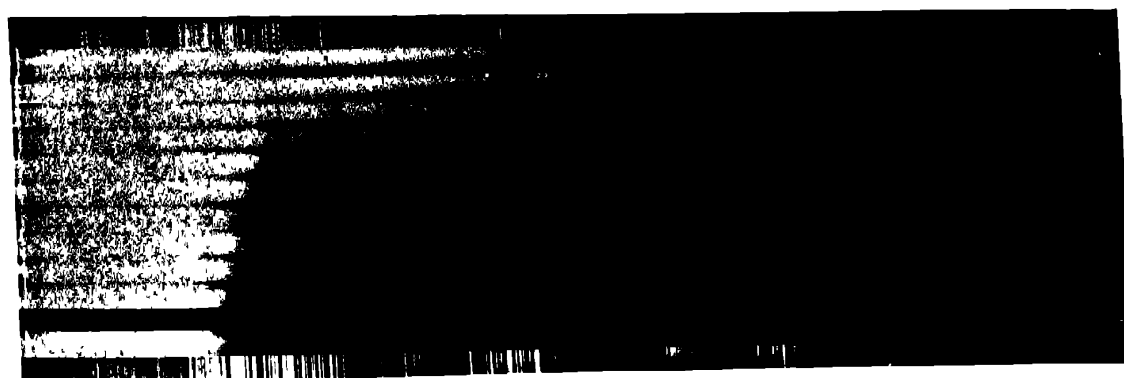
	Vapour			Solution		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
**	3190	31340	500	3220	31040	500
**	3140	31840	620	3170	31540	450
	3080	32160	420	3125	31990	470
	3040	32880	550	3080	32460	420
	2990	33430	460	3040	32880	440
	2950	33890	460	3000	33320	450
	2910	34350	480	2960	33770	470
	2870	34830	490	2920	34240	410
	2830	35320	510	2885	34650	490
	2790	35830	460	2845	35140	440
	2755	36290	400	2810	35580	
	2725	36690	470			
	2690	37160	560			
	2650	37720	430			



10 (b)



11 (a)



11 (b)

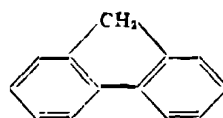
FIG. 10. Fluorene: (b) Solution.

FIG. 11. Fluoranthene. (a) Vapour, (b) Solution

TABLE 9—(Contd.)

	Vapour			Solution		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
	2620	38150				
			440			
	2590	38590				
			160			
	2560	39050				
			620			
	2520	39670				
			480			
	2490	40150				
			490			
	2460	40640				
			500			
	2430	41140				
			510			
	2400	41650				
			350			
	2380	42000				
			360			
	2360	42360				
			540			
	2330	42900				
			560			
	2300	42460				

10. *Fluorene*.

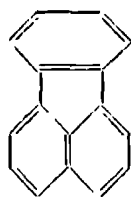


This substance also shows bands sharp on the ultra-violet side. There are also four or five well-defined equally spaced bands, clearly separated from the region of continuous absorption. See Figs 10 (*a*) and (*b*), Plates IX and X.

TABLE 10.

Int.	Vapour			Solution			Solid		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
3	3675	27200		3735	26770		3845	26000	
			410 \uparrow			400 \uparrow			110 \uparrow
1	3620	27610	1440	3680	27170	1390	3785	26410	1420
			\downarrow			\downarrow			\downarrow
3	3490	28610		3550	28160		3645	27420	
			420 \uparrow			360 \uparrow			390 \uparrow
1	3440	29060	1470	3505	28520	1460	3595	27810	1510
			\downarrow			\downarrow			\downarrow
3	3320	30110		3375	29620		3455	28930	
			410 \uparrow			400 \uparrow			390 \uparrow
1	3275	30520	1420	3330	30020	1570	3410	29320	1550
			\downarrow			\downarrow			\downarrow
3	3170	31530		3205	31190		3280	30480	
			410 \uparrow			300 \uparrow			330 \uparrow
1	3130	31940	1470	3175	31490	1370	3245	30810	1360
			\downarrow			\downarrow			\downarrow
3	3030	33000		3070	32560		3140	31840	
			720 \uparrow			760 \uparrow			
9	2965	33720		3000	33320				
			170 \uparrow						
6	2950	33890							
			350 \uparrow			1500 \uparrow			
3	2920	34240	1470						
			\downarrow			\downarrow			
8	2900	34470	230	2935	34060				
			\uparrow			470 \uparrow			
6	2860	34950	180	2895	34530				
			500 \uparrow			1390 \uparrow			
6	2820	25450	1550						
			\downarrow			\downarrow			
5	2775	36020	570	2820	35450				
			\downarrow						
5	2740	36480	460						
			\downarrow						
4	2710	36890	410	2770	36090				
			\downarrow			590 \downarrow			
3	2685	37230	340	2725	36680				
			\downarrow						
3	2655	37650	420						
			\downarrow						
3	2605	38370	720						
			\downarrow						
3	2550	39200	830	2640	37870				
			\downarrow			360 \downarrow			
3	2500	39990	790	2615	38230				
			\downarrow			820 \downarrow			
3	2460	40640	650	2560	39050				

11. Fluoranthene.



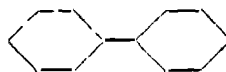
The spectrum resembles that of fluorene, but is much richer in bands. See Figs. 11 (a) and (b), Plate X.

TABLE 11 Absorption spectrum of fluoranthene (Benzo-acenaphthene).

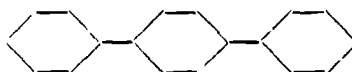
Int.	Vapour			Solution		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
6	3510	28480		3585	27890	
			750 \uparrow			\uparrow
3	3420	29230	1450			1470
			700 \downarrow			\downarrow
6	3340	29930		3405	29360	
			740 \uparrow			\uparrow
3	3260	30670	1460			1490
			720 \downarrow			\downarrow
6	3185	31390		3240	30850	
			1440			1500
3	3045	32830		3090	32350	
			1410			1480
4	2920	34240		2955	33830	
			710 \uparrow			\uparrow
2	2860	34950	1270			1000
			560 \downarrow			\downarrow
9	2815	35510		2870	34830	
			510 \uparrow			
7	2775	36020				
			600 \uparrow		680	
6	2730	36620	1450			
			\downarrow			
8	2705	36960		2815	35510	
			450 \uparrow			
5	2665	37410				710
			460 \uparrow			
5	2640	37870	1420			
			510 \downarrow			
5	2605	38380		2760	36220	
			370			600
5	2580	38750		2715	36820	
			380			
5	2555	39130				1480
			380			

TABLE 11—(Contd.)

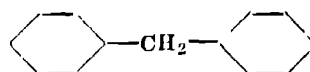
Int.	Vapour			Solution		
	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
5	2530	39510		2610	38300	
			480			
3	2500	39990				1240
			650			
3	2460	40640		2525	39540	
			750			1260
2	2415	41390		2450	40800	

12. *Diphenyl.*

The spectrum shows no banded structure, and is in striking contrast to that of benzene or naphthalene

13. *Terphenyl.*

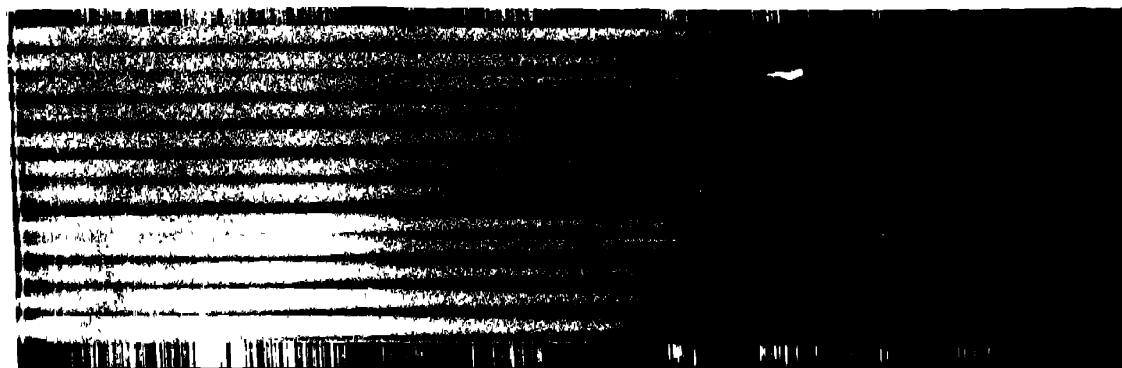
The spectrum is similar to that of diphenyl with no indication of a band system.

14. *Diphenylmethane*

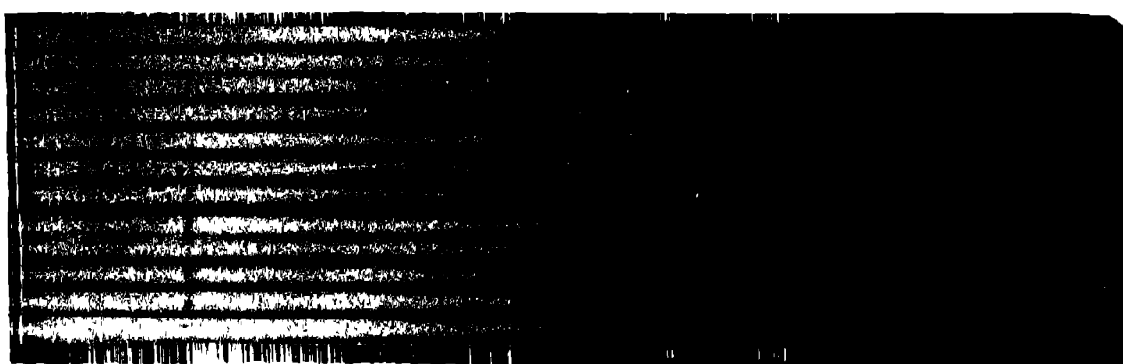
The continuous absorption spectrum is similar to that of diphenyl; there appear, however, five or six bands spaced at intervals of 450 cm^{-1} , which are absent from the spectrum of diphenyl. See Figs 12 (a) and (b) Plate XI.

TABLE 12 Absorption spectrum of diphenylmethane

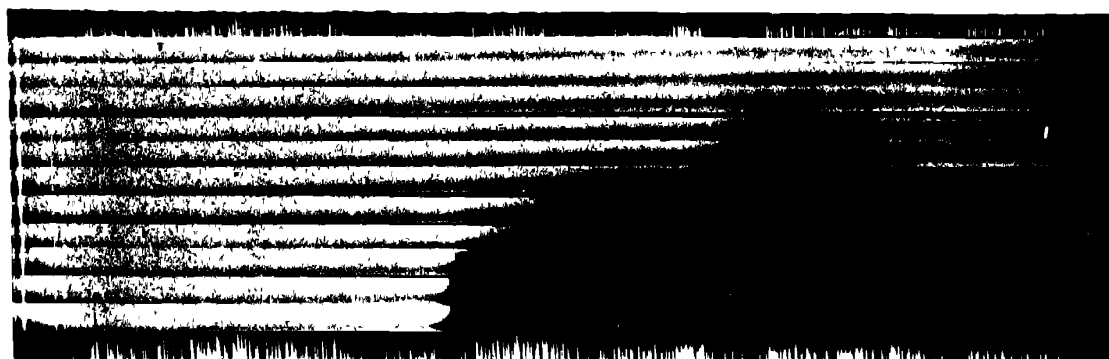
Vapour			Solution		
λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
2670	37440		2695	37080	
		430			400
2640	37870		2665	37480	
		430			460
2610	38300		2635	37940	
		450			510
2580	38750		2600	38450	
		470			440
2550	39220		2570	38890	
		450			460
2520	39670		2540	39350	
		400			400
2495	40070		2515	39750	



12(a)



12(b)



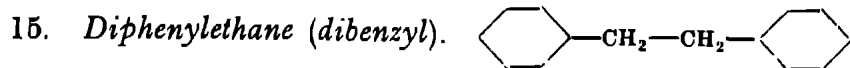
13(a)



13(b)

FIG. 12.—Diphenylmethane (a) Vapour, (b) Solution.

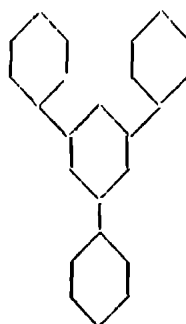
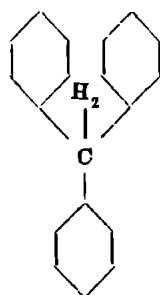
FIG. 13.—Dibenzyl (a) Vapour, (b) Solution.



The absorption spectrum resembles that of diphenylmethane See Figs. 13 (a) and (b), Plate XI.

TABLE 13.
Absorption spectrum of dibenzyl.

Vapour			Solution		
λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
2690	37160		2715	36820	
		420			480
2660	37580		2680	37300	
		430			420
2630	38010		2650	37720	
		440			440
2600	38450		2620	38160	
		450			440
2570	38900		2590	38600	
		460			450
2540	39360		2560	39050	
		390			460
2515	39750		2530	39510	
		480			470
2485	40230		2500	39980	
		410			410
2460	40640		2475	40390	



These substances again show no banded absorption in the region investigated.

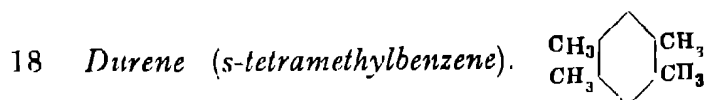
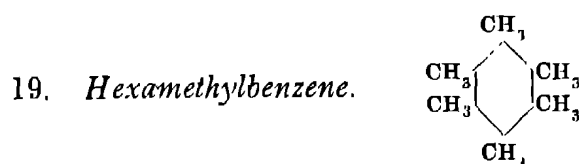


TABLE 14
Absorption spectrum of durene.

Vapour		
λ	ν	$\Delta\nu$
2780	35970	
		660
2730	36630	
		680
2680	37310	
		710
2630	38020	



Here again there is no banded absorption

4. Analysis of the Absorption Bands.

A complete analysis of the absorption spectrum of such complicated molecules is naturally difficult, but as was mentioned in the introduction, some of the molecular constants, as for example, the vibrational frequencies in the initial and excited states, and the electronic frequencies, can be readily obtained. To a first approximation if we neglect the rotational fine-structure and also the anharmonicity of the vibrations, we can represent the frequencies of the various absorption bands by the simple formula

$$\nu = \nu_e + m\alpha + n\beta + \dots p\alpha_0 - q\beta_0 - \dots \quad (1)$$

where ν_e is the frequency corresponding to the transition from the zero vibrational level of the normal molecule to a similar level of the excited molecule, α, β, \dots are the vibrational frequencies of the excited molecule, and α_0, β_0, \dots are the vibrational frequencies of the normal molecule, m, n, \dots, p, q, \dots are simple integers. There is one striking difference between the values of the vibrational quantum numbers m, n, \dots characteristic of the excited molecule, and those of p, q, \dots characteristic of the normal molecule, occurring in (1). Whereas m, n, \dots can assume any value from zero up to large numbers, the quantum numbers p and q can assume small values only, usually 0, 1, and 2. This is conditioned by the fact that the intensity of any absorption

band corresponding to a given value of p will be proportional to the population of the molecules which are normally in the p th vibrational state, and the number of molecules in the different vibrational states $p = 0, p = 1, \dots$ should, according to the Boltzmann distribution, be in the ratio

$$1 : e^{-\epsilon/kT} : e^{-2\epsilon/kT} : \dots\dots\dots,$$

where $\epsilon = hca_0$. Taking T as $300^\circ K$ (the temperature of the room), and a_0 to be of the order of 400 cm.^{-1} (which, as we shall see presently, is of the order of magnitude of the vibrational frequencies of these molecules in the normal state), the above ratios would be equal to $1 : 1/7 : 1/50$; so that the number of molecules present even in the second vibrational state would be quite small, namely, $1/50$, while those present in the higher vibrational levels would be negligible.

This circumstance enables us to distinguish the vibrational frequencies characteristic of the normal molecule, namely, α_0, β_0, \dots from the frequencies α, β, \dots characteristic of the molecule in the higher electronic level. Whereas the former frequencies are repeated only once or twice, the latter appear in regular succession.

Taking for example anthracene, it is easy to see, using this criterion, that there is only one prominent frequency for the excited molecule, equal to 1450 cm.^{-1} (See Table 2) and one for the normal molecule, equal to 400 cm.^{-1} and the various absorption frequencies are therefore expressed by the simple equation

$$\nu = 27540 + n \times 1450 - p \times 400 \quad \dots \quad \dots \quad \dots \quad (2)$$

For the other molecules also the vibrational and the electronic frequencies can be obtained in the same manner, and their values are collected together in Table 15.

5 *Absorption Spectra in Relation to Molecular Structure.*

The absorption spectrum, as is well known, is very sensitive to changes in molecular structure. For example, when we pass from benzene to durene (*s*-tetramethylbenzene), practically all the wealth of details that we observe in the spectrum of benzene vapour disappears, and in hexamethylbenzene there is not even an indication of a banded structure. The same effect is strikingly brought out in the spectra of diphenyl, *p*-diphenyl benzene, triphenyl benzene and triphenyl methane, none of which shows any banded absorption, in spite of the fact that the benzene rings in these compounds have the same structure as in the benzene molecule. On the other hand, diphenylmethane and diphenylethane show a diffuse band structure.

When the benzene rings, instead of being discrete as in diphenyl or triphenyl, fuse together so as to form naphthalene or anthracene or

TABLE 15. *Molecular Frequencies.*

No.	Molecule	ν	Vibrational Frequency			
			Excited Molecule		Normal Molecule	
			α	β	α_0	β_0
1	Naphthalene ..	31320	420		230	
2	Anthracene ..	27540	1450		400	
3	Naphthacene ..	22220	1400		400	
4	Phenanthrene ..	27540	1450		720	350
5	Chrysene ..	27730	1300	1400	600	400
6	Dibenzanthracene .		1300		700	400
7	Pyrene ..	27540	1450		300	500
8	Perylene ..	24030	1450		480	
9	Acenaphthene ..	31340	400		280	
10	Fluorene ..	27200	1450		400	
11	Fluoranthene ..	28480	1450		700	350
12	Diphenylmethane ..	37160	450			
13	Dibenzyl ..	37440	450			

phenanthrene, the absorption spectrum is very rich in bands. On the basis of the general character of the absorption spectrum, the condensed-nuclear compounds may be divided into the following groups:—(1) compounds like naphthalene, anthracene and naphthacene in which the benzene rings are arranged linearly; they all have sharp absorption bands whose intensities follow in a general manner the intensities of the continuous spectrum of absorption accompanying them; the two regions of absorption are clearly marked; (2) pyrene and perylene, with close-packed condensed nuclei; they have more or less the same characteristics as compounds (1); (4) compounds like phenanthrene, chrysene and dibenzanthracene; the two regions of absorption are not so well defined as in (1) and (2), and the progression of intensities of the bands is also different; (4) molecules with incomplete rings, as acenaphthene, fluorene and fluoranthene; the bands are quite sharp and are crowded in

a small region of the spectrum ; most of these bands have sharp edges on the short-wave-length side, while they shade gradually on the long-wave-length side ; some of the absorption bands of naphthalene also have this characteristic

Considering the different molecules in the same group, the band spectrum becomes more and more diffuse as we go to the higher members, and moreover shifts continually towards the red end of the spectrum. For example, naphthalene spectrum shows a number of fine-structure details, which are absent from that of either anthracene or naphthacene ; as we pass from naphthalene to anthracene, the absorption bands shift towards the red by about 4970 cm^{-1} , and again by 5320 cm^{-1} when we pass from anthracene to naphthacene ; (See Table 15)

In connection with the Table 15, we should also remark that the vibrational frequencies, both of the excited and of the normal molecules, are practically of the same magnitude for all the compounds. This is not surprising since the vibrational frequencies of a molecule are not so sensitive to changes in its structure as its electronic frequencies are, as we know from Raman and infra-red investigations on organic substances.

We mentioned in an earlier section that the influence of the physical state on the absorption spectrum is a general broadening of the bands, and consequent loss of fine details, as the medium gets dense, and a lateral shift of the band system towards the red, *relative positions of the components of the band system remaining practically unaffected*. These results are clearly seen from the tables of the absorption spectra for the different physical states, and from the spectrograms reproduced ; they suggest that the *vibrational* frequencies $\alpha, \beta, \dots, \alpha_0, \beta_0, \dots$ of the molecules are practically the same in the different physical states, but their *electronic* frequencies ν_e show a progressive diminution as we pass from the vapour to the solution and thence to the solid state.

Summary.

Several aromatic hydrocarbons have been studied for their absorption spectra in the vapour state over the spectral range 7000 \AA to 2200 \AA . A general analysis is made of the band systems, and the values of vibrational frequencies of the molecules in the normal and in the excited states, and of the electronic frequencies of the molecules, are calculated therefrom. These frequencies are discussed in relation to the structure of the molecules, and in relation to their physical states of aggregation.

The author desires to express his thanks to Prof. K. S. Krishnan for his guidance and keen interest in the progress of this work.

THE ABSORPTION SPECTRA OF SOME AROMATIC COMPOUNDS.

Part II. Quinones and Hydroquinones.

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Received December 29, 1935.

(Communicated by Prof K S Krishnan, D Sc)

1. Introduction.

THE absorption spectra of quinones and hydroquinones are of great interest from the point of view of their molecular structure. Among these compounds only benzoquinone has been studied in detail, by Purvis,¹ Lifschitz and Rosenbohm,² and more recently by Louis Light,³ and the spectrum shows a number of interesting features. Some preliminary work has been done on naphthoquinone and anthraquinone. Hydroquinone has been studied in solution only, in which state it shows some broad regions of absorption. We have therefore studied the absorption spectra of vapours of quinhydrone, hydroquinone, phloroglucinol, 1,4-naphthoquinone, 9,10-anthraquinone, 9,10-phenanthraquinone, β -hydroxyanthraquinone and naphthazarin (5,8-dihydroxy-1,4-naphthoquinone), in some detail, from 7000 to 2200 Å, with a spectrograph of high dispersion: we have also extended the studies on *p*-benzoquinone further into the ultra-violet than has been done previously. The present paper gives an account of these investigations.

These substances have been studied by us in other physical states also, *e.g.*, in a state of solution in suitable solvents, and sometimes also in the solid state. The influence of the physical state on the absorption is discussed

2. Experimental.

A water-cooled hydrogen discharge tube, specially designed to give large intensity,⁴ served as the source of continuous radiation in the ultra-violet for the various absorption experiments. In the near ultra-violet and in the visible regions, however, this source was not quite so convenient,

¹ *Jour. Chem. Soc.*, 1923, 123, 1841.

² *Zeits. f. Phys.*, 1926, 38, 61

³ *Zeits. f. Phys. Chem.*, 1926, 122, 414

⁴ *Jour. Sci. Instruments*, 1935, 12, 260.

since it gave some intense *lines* as well. For these regions a tungsten linear filament lamp, fitted with a quartz window, was found to be very suitable.

The absorption spectra were in general photographed with a Hilger E₁ quartz spectrograph giving a large dispersion. For very diffuse bands, however, a smaller dispersion was desirable, and the Hilger E₂ was used.

The absorption tube was 75 cms. long, closed at both ends by quartz plates. It was placed in a convenient air oven, in which the whole tube could be heated and maintained at any desired temperature up to 300° C. by regulating the supply of the heating gas. The light from the source was collimated with the help of a quartz lens, and after passage through the absorption tube was condensed by another quartz lens on the slit of the spectrograph.

All the substances studied were solids at room temperature. They were either Merck's or Kahlbaum's pure products, which were further purified by sublimation or recrystallisation. They were placed inside the absorption tube, and the temperature was raised in stages of 10° C., and the absorption spectra were photographed. The absorptions would correspond to the *saturation* vapour pressures of the substances at the respective temperatures. An iron arc, photographed in juxtaposition with the absorption spectra, served for the measurements of wave-lengths.

3. *Description of the Absorption Spectra.*

Benzoquinone—With the lowest vapour pressure, *viz*, the saturation vapour pressure at laboratory temperature, the absorption of benzoquinone is almost negligible up to 2450 Å, beyond which there appears a set of nine or ten broad equally-spaced bands extending up to 2250 Å (see Fig. 1 a, Plate XII). The constant interval between the bands is about 450 cm⁻¹. Beyond 2250 Å, the absorption *diminishes* slightly, though this is not brought out in the spectrograms reproduced in the figure, owing to the rapid enfeebling of the incident light from the hydrogen tube at about this region, but the diminution of absorption beyond 2250 Å is clear in photographs taken with long exposures. We shall refer, for simplicity, to this region of absorption, from 2250 to 2450 Å, as region I.

As the temperature of the absorption tube is increased to about 60–70° C., and consequently the vapour pressure also, a second region of absorption, extending from 2600 to 3150 Å, appears. The bands in this region, which we shall refer to as Region II, are less diffuse than those in region I. They consist of two sets of equally-spaced bands having the same spacing as in I, *viz*, 450 cm⁻¹, the two sets being displaced relatively to each other by 230 cm⁻¹.

TABLE 1. *p*-Benzoquinone,
Regions I and II. $\nu = 31780 + 450 n - 230 p$.

<i>n</i>	<i>p</i>	ν calculated	λ calculated	λ observed	Intensity <i>p</i> =0 <i>p</i> =1	
			<i>Region II.</i>			
0	0	31780	3146	3145	0	
1	1	32000	3124	3125		0
1	0	32230	3102	3103	1	
2	1	32450	3080	3081		0
2	0	32680	3059	3059	2	
3	1	32900	3038	3038		1
3	0	33130	3017	3018	3	
4	1	33350	2997	2998		3
4	0	33580	2977	2978	4	
5	1	33800	2957	2957		5
5	0	34030	2937	2937	5	
6	1	34250	2919	2917		6
6	0	34480	2899	2899	6	
7	1	34700	2881	2880		7
7	0	34930	2862	2861	7	
8	1	35150	2844	2844		8
8	0	35380	2825	2826	8	
9	1	35600	2808	2807		8
9	0	35830	2790	2790	8	
10	1	36050	2773	2774		7
10	0	36280	2755	2756	7	

TABLE 1 (contd.)

n	p	ν calculated	λ calculated	λ observed	Intensity $p=0$ $p=1$
11	1	36500	2738	2740	5
11	0	36730	2722	2723	5
12	1	36950	2705	2705	3
12	0	37180	2689	2690	3
13	1	37400	2673	2672	2
13	0	37630	2656	2655	3
14	1	37850	2641	2640	1
14	0	38080	2625	2628	2
15	0	38530	2594	2595	1
16	0	38980	2564	2560	0
17	0	39430	2535	2530	0
<i>Region I.</i>					
18	0	39880	2507	2505	3'
19	0	40330	2479	2480	3'
20	0	40780	2451	2450	3'
21	0	41230	2425	2425	4'
22	0	41680	2398	2395	5'
23	0	42130	2373	2390	6'
24	0	42580	2348	2350	6'
25	0	43030	2323	2320	4'
26	0	43480	2299	2295	4'
27	0	43930	2276	2280	3'
28	0	44380	2253	2255	2'

With further increase of temperature, *viz.*, to 85–95° C., a third region of absorption appears, which extends from 4100 to 4750 Å. The absorption bands in this region, III, are very sharp, unlike those in regions I and II, and are accompanied by a number of fine structure components, which are more or less equally spaced ($\Delta \nu \sim 35 \text{ cm.}^{-1}$)

The positions of the ultra-violet bands of benzoquinone and their intensities in arbitrary units are given in Table 1. The significance of the different columns in the table will be clear from the next section. The intensities for the two series $p = 0$, and $p = 1$ are tabulated in different columns, so as to enable the progression of intensities of the two series to be followed separately. Since the bands in region I were photographed at much lower vapour pressures than those corresponding to region II, a different standard of intensity, indicated by dashed numbers, has been adopted for I. The wave-numbers in this and in the following tables are all expressed in cm.^{-1} (For the absorption bands of benzoquinone in the *visible region* see Table 3)

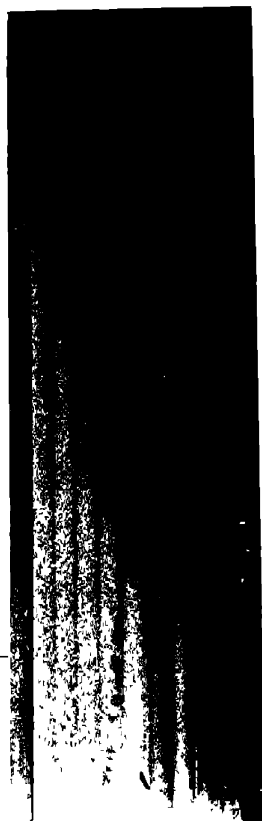
Hydroquinone—There are two prominent regions of absorption, both of which are in the ultra-violet (see Fig 2a, Plate XII) :

(1) From 2300 to 2500 Å, consisting of diffuse bands spaced at intervals of 420 cm.^{-1} , which are very similar to those of *p*-benzoquinone in region I; this region appears at about 100° C.

(2) The second region appears at about 130° C and extends from 2500 to 3050 Å ; it consists of about 15 bands having the same spacing as in region I, *viz.*, 420 cm.^{-1} ; they are, however, much sharper than those in region I, and are accompanied by two or three fine structure components on either side at intervals of 30 cm.^{-1} . The benzoquinone bands in this region do not show this fine structure (see Figs. 9a and 9b, Plate XIV) Besides this main set of bands, there are two other sets of bands in this region having the same spacing of 420 cm.^{-1} as the main set, and displaced with reference to the latter by about 295 and 170 cm.^{-1} respectively towards the larger wavelength side. These bands are very faint compared with the main set, and, even with high vapour pressures, only the early members could be observed ; the bands shifted by 170 cm.^{-1} are feebler than those shifted by 295 cm.^{-1} . The positions of these bands are given in Table 2.

As we have already mentioned, hydroquinone does not show any absorption bands in the visible region.

1(b)



2(b)



3(b)

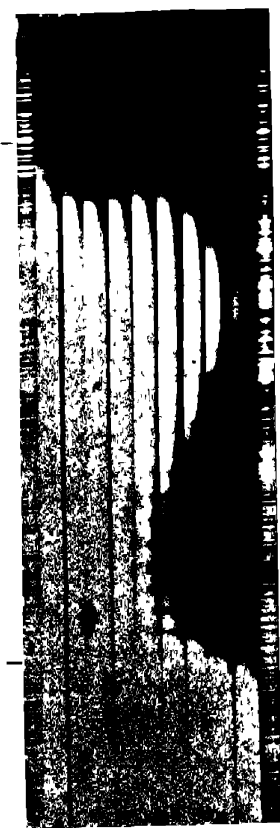


4(b)



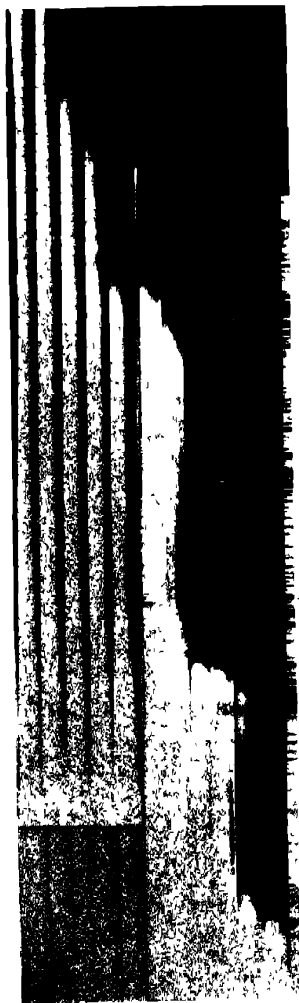
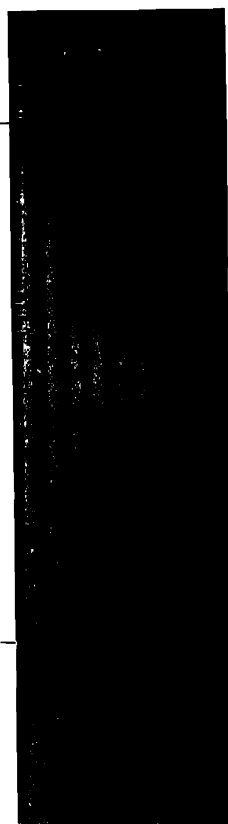
FIG 29414

3100





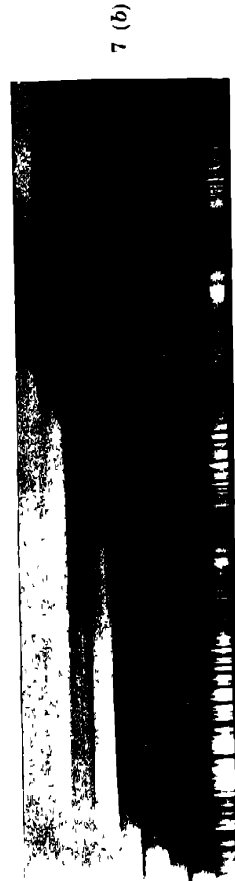
5 (b)



6 (a)



6 (b)



7 (b)

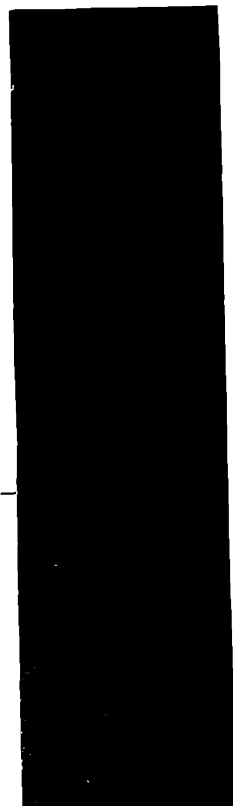
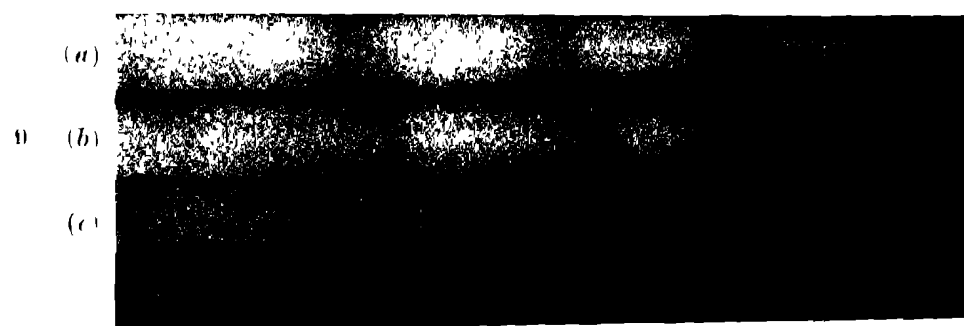


TABLE 2. *Hydroquinone.*
 $\nu = 33070 + 420 n - 295 p - 170 q.$

<i>n</i>	<i>p</i>	<i>q</i>	<i>ν</i> calculated	<i>λ</i> calculated	<i>λ</i> observed	Intensity		
						<i>p</i> =0 <i>q</i> =0	1 0	0 1
<i>Region II.</i>								
0	1	0	32775	3050	3050		2	
0	0	1	32900	3039	3040			1
0	0	0	33070	3023	3023	6		
1	1	0	33195	3012	3012		2	
1	0	1	33320	3000	3002			1
1	0	0	33490	2985	2984	7		
2	1	0	33615	2974	2972		2	
2	0	1	33740	2963	2962			1
2	0	0	33910	2948	2948	8		
3	1	0	34035	2937	2936		2	
3	0	1	34160	2926	2927			1
3	0	0	34330	2912	2912	9		
4	1	0	34455	2902	2902		2	
4	0	1	34580	2891	2891			1
4	0	0	34750	2877	2877	10		
5	1	0	34875	2866	2865		2	
5	0	1	35000	2856	2855			1
5	0	0	35170	2843	2843	10		
6	1	0	35295	2832	2830		2	
6	0	1	35420	2822	2820			1
6	0	0	35590	2809	2809	9		

TABLE 2—(contd.)

<i>n</i>	<i>p</i>	<i>q</i>	ν calculated	λ calculated	λ observed	Intensity		
						$p=0$ $q=0$	1 0	0 1
7	1	0	35715	2799	2799		2	
7	0	1	35840	2789	2789			1
7	0	0	36010	2776	2776	8		
8	1	0	36135	2767	2765		2	
8	0	0	36430	2744	2744	7		
9	0	0	36850	2713	2712	7		
10	0	0	37270	2682	2680	6		
11	0	0	37690	2652	2650	6		
12	0	0	38110	2623	2625	5		
13	0	0	38530	2594	2595	4		
14	0	0	38950	2566	2565	3		
15	0	0	39370	2539	2540	2		
<i>Region I.</i>								
16	0	0	39790	2512	2512	1'		
17	0	0	40210	2486	2490	1'		
18	0	0	40630	2461	2460	2'		
19	0	0	41050	2435	2930	3'		
20	0	0	41470	2411	2410	4'		
21	0	0	41890	2386	2390	5'		
22	0	0	42310	2363	2360	5'		
23	0	0	42730	2339	2340	5'		
24	0	0	43150	2317	2320	4'		



Quinhydrone.—The absorption bands in the visible region, given in Table 3, are identical with those of benzoquinone even as regards the finer details. This is brought out clearly in Fig. 10, Plate XIV, where the absorption spectra of these two substances for a small region are exhibited side by side.

The absorption bands of quinhydrone in the ultra-violet are given in Table 4. All the bands that are observed are explicable as being due to either benzoquinone or hydroquinone. (This will be clear from Fig. 8, Plate XIV, which gives the bands in the ultra-violet in juxtaposition with those of *p*-benzoquinone on one side, and those of hydroquinone on the other. Fig. 9 is a similar picture taken under a higher dispersion referring to a small region in the ultra-violet.) The last column in the table indicates the origin of the various bands; the letter B signifies that the bands are due to benzoquinone, the subscripts 0 and 1 indicating whether they belong to the series $p = 0$ or $p = 1$. The letter H similarly indicates that the band is due to hydroquinone. Only the bands belonging to the series $p = 0, q = 0$, could be observed, the other two series, defined by $p = 0, q = 1$, and $p = 1, q = 0$, being too weak to appear.

It is clear from these Tables and also from Figs. 8, 9, 10, Plate XIV, where the bands of all the three compounds are exhibited side by side, *that the absorption spectrum of quinhydrone can be treated as the superposition of the spectra of benzoquinone and hydroquinone.*

4 Analysis of the Bands.

Neglecting, for convenience in discussion, the rotational fine structure, and also the small anharmonic corrections for the vibrations, we may, following Henri⁵ and others, represent the frequencies of the various components of a band-system by a formula of the type

$$\nu = \nu_e + m\alpha + n\beta + \dots - p\alpha_0 - q\beta_0 - \dots \quad \dots (1)$$

where ν_e is the electronic frequency corresponding to the transition from the zero vibrational state of the normal molecule to a similar state of the excited molecule. α, β, \dots are the vibrational frequencies characteristic of the excited molecule, and similarly α_0, β_0, \dots of the normal molecule. The quantum numbers p and q which refer to the vibrations in the initial state, can have only small values, *viz.*, 0, 1, since the population of the molecules normally occupying the higher vibrational states will be negligible. On the other hand, the quantum numbers m, n , etc., defining the vibrations in the final state, *i.e.*, of the excited molecule, can naturally assume large values.

⁵ *Jour. de Chim. Phys.*, 1935, 32, 353, and previous papers. See also *Tables Annuelles de Constantes*, Paris, 1930.

TABLE 3.

Absorption bands of quinhydrone in the visible (identical with those of p-benzoquinone).

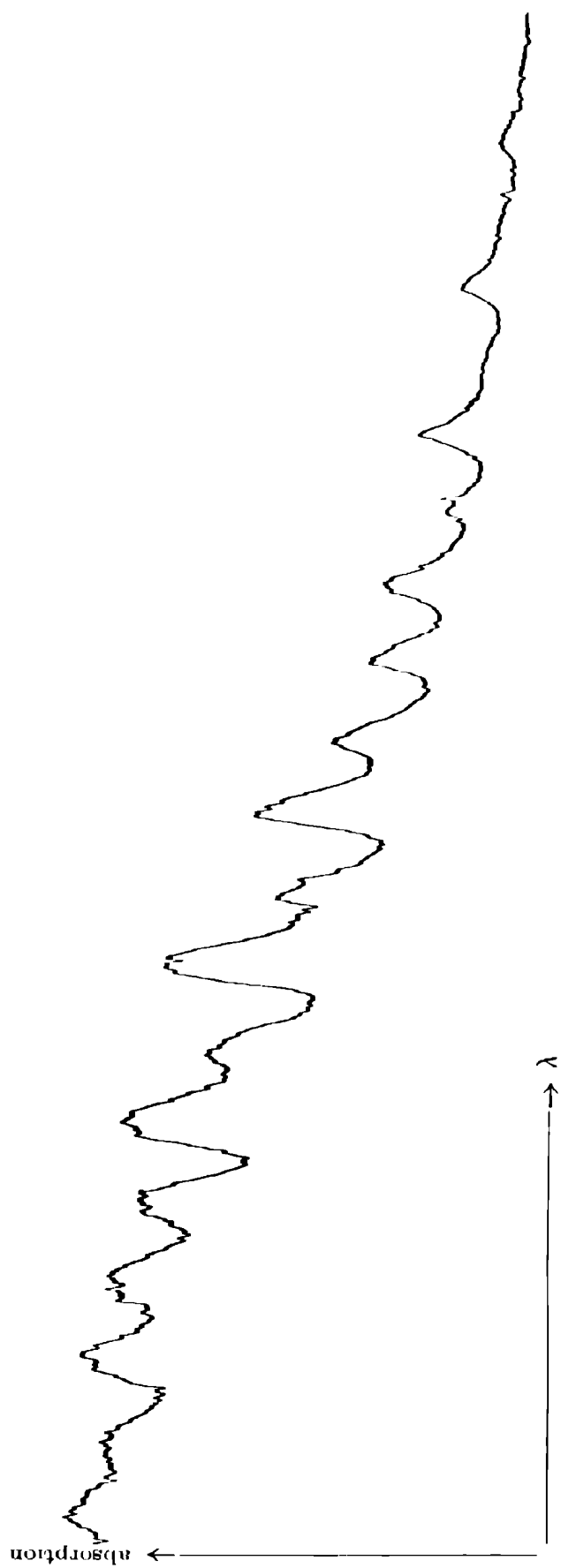
λ	Int
4766.2	25
4758.4	17
4750.3	17
4742.0	12
4734.0	10
4557.5	3
4548.1	5
4537.4	25
4529.6	17
4521.9	15
4448.2	5
4440.5	7
4433.6	5
4378.2	5
4370.7	5
4362.7	6
4318.9	20
4312.2	17
4305.2	15
4297.5	12
4291.0	7
4237.6	5
4230.1	5
4224.0	5
4217.8	4
4173.4	3
4166.4	2
4159.8	2

TABLE 4.

Absorption bands of quinhydrone in the ultra-violet.

λ	Int	Origin
3100	1	B ₀
3060	2	B ₀
3038	3	B ₁
3023	3	H
3017	3	B ₀
2997	4	B ₁
2985	4	H
2979	5	B ₀
2968	5	H
2957	5	B ₁
2948	5	H
2937	6	B ₀
2918	6	B ₁
2912	6	H
2900	7	B ₀
2880	7	B ₁ , H
2860	8	B ₀
2845	8	B ₁ , H
2825	7	B ₀
2810	7	B ₁ , H
2790	6	B ₀
2775	6	B ₁ , H
2755	5	B ₀
2740	5	B ₁ , H
2720	4	B ₀
2710	4	B ₁ , H
2690	3	B ₀
2655	3	B ₀ , H
2510	2'	B
2480	3'	B
2450	3'	B
2430	5'	B, H
2400	6'	B, H
2375	6'	B, H
2355	5'	B, H
2330	4'	B, H
2305	3'	B, H

Benzoquinone.—Let us first consider the ultra-violet bands of benzoquinone. From the occurrence of numerous bands at regular intervals of



450 cm.⁻¹, over the entire regions I and II, it is plain that this should be a vibrational frequency of the excited molecule; moreover, there is no other such frequency. It is further clear from Table 1 that for the normal molecule also there is only one vibrational frequency, which should be equal to the relative displacements of the two sets of equally-spaced bands. This displacement, in cm.⁻¹, is either 230, or 230 + 450 or again 230 + 2 × 450, none of which is *a priori* improbable. A unique choice between the three alternatives can be made if we can fix definitely the origins (long wave-length limits) of the two sets of bands. As can be seen, however, from the microphotograph* exhibited in Fig. 12, Plate XV, and also from the intensity values given in Table 1, the intensities of both the sets fall off rapidly near the long wave-length end, so that it is very difficult to fix definitely the first band of either series. We shall provisionally adopt 230 cm.⁻¹ as the vibrational frequency of the normal molecule and write the general formula in the form

$$\nu = 31780 + n \times 450 - p \times 230 \quad \dots \quad (2)$$

$n = 0, 1, 2, \dots, 28$; $p = 0, 1$; though, as we have mentioned, the alternative expressions

$$\nu = 32230 + n \times 450 - p \times 680 \quad \dots \quad (3)$$

$$\text{and } \nu = 32680 + n \times 450 - p \times 1130 \quad \dots \quad (4)$$

are not excluded. Data for the infra-red and the Raman spectra for the compound, which at present are not available, may enable us to decide between them.

In region II both the series, corresponding to $p=0$ and $p=1$ respectively, appear, the latter being fainter, as we should expect; beyond 2500 Å, however, *i.e.*, when we pass from region II to region I, the series $p=1$ fades out, and only that corresponding to $p=0$, *i.e.*, to transitions from the initial zero vibrational states continues to appear, though more diffusely than in region II.

The bands of benzoquinone in the visible region are more difficult to analyse, because of the fewer repetitions of the vibrational spacing and the appearance of numerous rotational components of more or less the same intensity. The rotational frequency is, however, uniquely determined, and is equal to 35 cm.⁻¹. This would correspond to a moment of inertia of $0.8\% \times 10^{-40}$ which is of the proper magnitude.

Hydroquinone—In hydroquinone also there is only one vibrational frequency for the excited molecule, *viz.*, 420 cm.⁻¹. For the normal molecule, however, there are two frequencies 170 and 295 cm.⁻¹, the former being

* My thanks are due to Dr. I. R. Rao of the Andhra University for the microphotometric records.

feebler than the latter. The general expression for the band frequencies can be written in the form

$$\nu = 33070 + n \times 420 - p \times 295 - q \times 170, \quad \dots (5)$$

where n may have any value from 0 up to 25; p and q may be both zero or one of them may have a value 1: that is, in the initial state the molecule is either in the zero vibrational state or in the first vibrational state corresponding to either the 295 vibration or the 170 vibration. We should mention immediately that, just as in benzoquinone, owing to the difficulty in fixing the long wave-length limits of the three series, $n=0, p=0, q=0$; $n=0, p=1, q=0$; and $n=0, p=0, q=1$, the vibrational frequencies of the normal molecule may, instead of being 295 and 170 cm^{-1} , be equal to $290+420$ and $170+420$, or even $295+2 \times 420$ and $170+2 \times 420$. For these latter alternatives the values of ν , in expression (5) would have to be suitably adjusted.

As in benzoquinone, the series $p=1, q=0$, and $p=0, q=1$, appear only in region II. When we pass into region I, only the series $p=0, q=0$ persists.

The rotational satellites accompanying the earlier members of the series, which are absent in the corresponding bands of benzoquinone in this spectral region, give for hydroquinone nearly the same rotational frequency as for benzoquinone, *viz.*, 30 cm^{-1} .

Quinhydrone.—We need not make any special mention here of the analysis of the quinhydrone bands, since some of them are identical with those of benzoquinone and the remaining ones with those of hydroquinone, and thus fit with one or the other of the expressions (2) and (5).

5. Other Compounds.

Among the other compounds studied by us, we shall first consider the higher quinones, *viz.*, 1,4-naphthoquinone, 9,10-anthraquinone, and 9,10-phenanthraquinone. They show three or four broad regions of absorption, with their maxima in the positions indicated in Table 7. The absorption spectra taken with an E_2 spectrograph are exhibited in Plate XIII.

These absorption regions, on close examination, show details of a band system, whose positions are as given in Table 5.

Naphthazarin.—There are two regions of absorption, one in the ultra-violet, which is continuous, *i.e.*, without any details of a banded structure, and the other in the visible region, which is much stronger, and shows a set of well-defined bands in the following positions (Table 6). These bands do not have any rotational fine structure (see Fig. 11, Plate XIV).

TABLE 5.

1,4-Naphthoquinone			9,10-Anthraquinone			9,10-Phenanthraquinone		
λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$
	I			I			I	
3450	28980		3300	30300		4095	24420	
		420			460			450
3400	29400		3250	30760		4020	24870	
		440			480			440
3350	29840		3200	31240		3950	25310	
		450			390			420
3300	30290		3160	31630		3885	25730	
		470			410			440
3250	30760		3120	32040		3820	26170	
		480			420			
3200	31240		3080	32460				
	II			II			II	
						3295	30350	
								410
2490	40150		2660	37580		3250	30760	
		490			430			480
2460	40640		2630	38010		3200	31240	
		500			440			500
2430	41140		2600	38450		3150	31740	
					370			460
			2575	38820		3105	32200	
					380			
			2550	39200				
					400			
			2525	39600				
							III	
						2675	37370	
								430
						2645	37800	
								430
						2615	38230	
							IV	
						2465	40550	
								420
						2440	40970	
								510
						2410	41480	

TABLE 6.

λ	ν	$\Delta\nu$
5495	18190	585
5325	18775	655
5145	19430	310
5065	19740	335
4980	20075	325
4900	20400	320
4825	20720	330
4750	21050	335
4675	21385	

The absorptions of β -hydroxyanthraquinone and phloroglucinol do not show any band system at all

6 Discussion of Results

Of the various molecules studied, only benzoquinone and hydroquinone, which have the simplest structure, show any rotational fine structure. Indeed as we go to the higher quinones, besides the disappearance of the rotational fine structure, even the vibrational structure of the bands tends to fade away ; for example in naphtho-, anthra-, and phenanthra-, quinones only four or five early members of the vibrational series, corresponding to $n = 0$ to 5, could be detected. In phloroglucinol and the other hydroquinones even the vibrational structure is absent. We further find that, as the complexity of the molecule increases, the band system also shifts towards the visible region of the spectrum, as we should expect.

It is remarkable that the vibration frequency in the excited state is of the same magnitude for all the quinones and hydroquinones, *viz.*, 400-500 cm^{-1} .

Quinhydrone requires special mention here. It is generally regarded as a loose molecular compound of benzoquinone and hydroquinone. Its absorption, as we have seen, is found to be a superposition of the absorption spectra of benzo-, and hydro-, quinones. Since the absorption measurements were made at high temperatures, *viz.*, above 100° C., it is difficult to say

whether the superposed absorption spectrum that is observed is actually characteristic of quinhydrone, or of the benzoquinone and hydroquinone into which quinhydrone, may dissociate. The latter alternative seems to be more probable.

7. Other Physical States

In order to find the influence of the physical state of the substance on its absorption spectrum, we have studied also the absorption of these substances in a state of solution in alcohol, and, when the absorption was not too strong, in the solid state as well. The solution absorptions were studied in the usual manner, with a Baly's tube (see Figs marked (b) in Plates XII and XIII). The positions of the maxima of absorption in the different states are given in the following table:—

TABLE 7

1. Benzoquinone	..	Solid	4960			
		Solution	4700	2950	2440	
		Vapour	4300	2790	2390	
2 Hydroquinone	..	Solid	3010			
		Solution	2930	2420		
		Vapour	2840	2390		
3. 1,4-Naphthoquinone	..	Solution	3230	2620	2450	
		Vapour	3190	2480	2380	
4. 9,10-Anthraquinone	..	Solution	3340	2660	2420	
		Vapour	3130	2570	2370	
5. 9,10-Phenanthraquinone	..	Solution	4270	3260	2640	2560
		Vapour	3770	3050	2580	2440
6. β -Hydroxyanthraquinone		Solution	4710	3720	2730	2420
		Vapour		3120	2500	2300

There are two main results to which we may refer in this place : (1) In solution the vibrational and the rotational structures of the bands are completely quenched, even with the simple molecules, *viz.*, benzoquinone and hydroquinone, which show them conspicuously in the vapour state. (2) The positions of maxima for the solutions are shifted towards the longer wave-lengths with reference to the absorption by the vapour. As we pass from the solution to solid there is a further large shift towards longer wave-lengths. These results show that close proximity of other molecules, whether of the same kind as in the solids, or of a different kind as in the solutions, tends to shift

the absorption maxima towards the red end, and destroy the vibrational and rotational structures.

We have studied in great detail the absorption of naphthacene and a few other hydrocarbons in various physical states, in vapour state, in solution in different solvents, in solid solution and in the solid state, and the influence of the physical state on absorption will be discussed in a separate publication in connection with these studies.

8. *Summary.*

The absorption spectra of some quinones and hydroquinones in the vapour state have been studied over a wide spectral region, from 7000 to 2200 Å, with a high dispersion spectrograph. Many of them show a vibrational structure, and some of them also a rotational fine structure. The bands for the simplest of the molecules, namely benzoquinone and hydroquinone, have been analysed, and the characteristic vibrational frequencies of the normal and excited molecules have been determined. For the other molecules the vibrational frequencies for the excited state only could be so obtained.

The substances have been studied also in solution. The rotational and vibrational structures observed with the vapours are all quenched, and the maxima of absorption are considerably shifted towards the red end of the spectrum. In the solid state, in which also two of the substances were studied, there is a further shift of the absorption-maxima in the same direction.

The author desires to express his grateful thanks to Prof. K. S. Krishnan, for his guidance and interest in the work.

EXPLANATION OF THE PLATES.

The vapour absorption spectra were taken at intervals of 10°C between the temperatures indicated. The solutions were all in alcohol. The two iron lines indicated in the reference spectra in Plates XII and XIII are 3100 and 2414 Å.

PLATE XII.

1. Benzoquinone —(a) Vapour 30 to 110°C., (b) Solution.
2. Quinhydrone —(a) Vapour 60 to 130°C.; (b) Solution.
3. Hydroquinone.—(a) Vapour 80 to 150°C.; (b) Solution.
4. Naphthoquinone —(a) Vapour 80 to 170°C.; (b) Solution.

PLATE XIII.

5. Anthraquinone.—(a) Vapour 100 to 190°C.; (b) Solution.
6. Phenanthraquinone —(a) Vapour 140 to 240°C.; (b) Solution.
7. Hydroxyanthraquinone.—(a) Vapour 150 to 220°C.; (b) Solution.

PLATE XIV.

- 8 Vapour absorption by (a) hydroquinone; (b) quinhydrone, (c) benzoquinone.
- 9 Similar to 8 taken under a high dispersion to exhibit the fine structure of the bands:
(a) hydroquinone; (b) benzoquinone; (c) quinhydrone
10. Absorption in the visible region of naphthazarin vapour from 90 to 130°C.

PLATE XV.

11. Microphotometric record of benzoquinone vapour from 3100 to 2700 Å exhibit the progression of intensities of the two sets of bands

DIAMAGNETIC SUSCEPTIBILITY OF SULPHURIC ACID-WATER MIXTURE.

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Received February 5, 1936.

(Communicated by Prof. B. Venkatesachar, M.A., F.Inst.P.)

Introduction

IN this paper a study has been made of the diamagnetic susceptibility of sulphuric acid-water mixture Farquharson¹ has studied the same mixture with Curie-Cheneveau balance. His concentration susceptibility curve abounds in maxima and minima and deviates a good lot from the additive law. Varadachari² has also studied the same mixture. He infers the presence of definite hydrates in the solution. Till about 87% of the acid, the values of susceptibilities are less than the additive law and above 87% the values are above the additive law. Points of maximum deviation from the additive law are attributed to the formation of hydrates.

The apparatus in this investigation is the one devised by Sibaiya and Venkataramiah.³ " The test system of this apparatus consists of a pyrex-glass cylinder from which the opposite quadrants have been ground off. The grinding operation is done so as to obtain exact symmetry in the test-piece since any slight asymmetry would tilt it when immersed in a liquid. A thin glass stem fused to the test-piece along its axis, carries a plane mirror. The free end of the stem is attached to the lower end of a phosphor-bronze suspension, the upper end of which is attached to a brass rod. The test-system and the suspension are encased in a wide glass tube with an opening for cementing a lens, in front of the plane mirror. The torsion head is attached to the top of the glass tube. The liquid is inserted from a side tube. The tap at the bottom of the tube served to empty it after a completion of a set of readings. When the magnetic field is put on, the couple on the test-piece twists the suspension and the deflection of the image on the scale is noted. In order to obtain high sensitiveness the mirror on the test-piece is adjusted parallel to one of its ground faces, which in its zero position is

¹ *Phil. Mag.*, 1931, 12, 283.

² *Proc. Ind. Acad. Sci.*, Aug. 1935, 2, 161.

³ *Ind. Jour. Phys.*, 1932, 7, 393.

also parallel to the lines of force. The relation between the deflections obtained when the magnetic current is switched off and the volume susceptibility of the liquid is linear, thus rendering the calculation of the volume susceptibility very simple. A density determination enables one to calculate the specific susceptibility.

If the volume susceptibility of the material of the test-piece and the surrounding liquid be K_0 and K respectively the couple on the test-piece is $(K_0 - K) \int \frac{1}{2} (\Delta H^2 \times r) dv$ where dv_0 is the element of volume, whose position vector is r and H , the field intensity at the point. If C is the couple per unit twist and θ the angular deflection

$$K_0 - K = - \frac{C\theta}{\int \frac{1}{2} (\Delta H^2 \times r) dv} = - \lambda\theta$$

whence $K = K_0 + \lambda\theta$

and it is clear that K and θ are linearly connected and that K_0 is obtainable by interpolation "

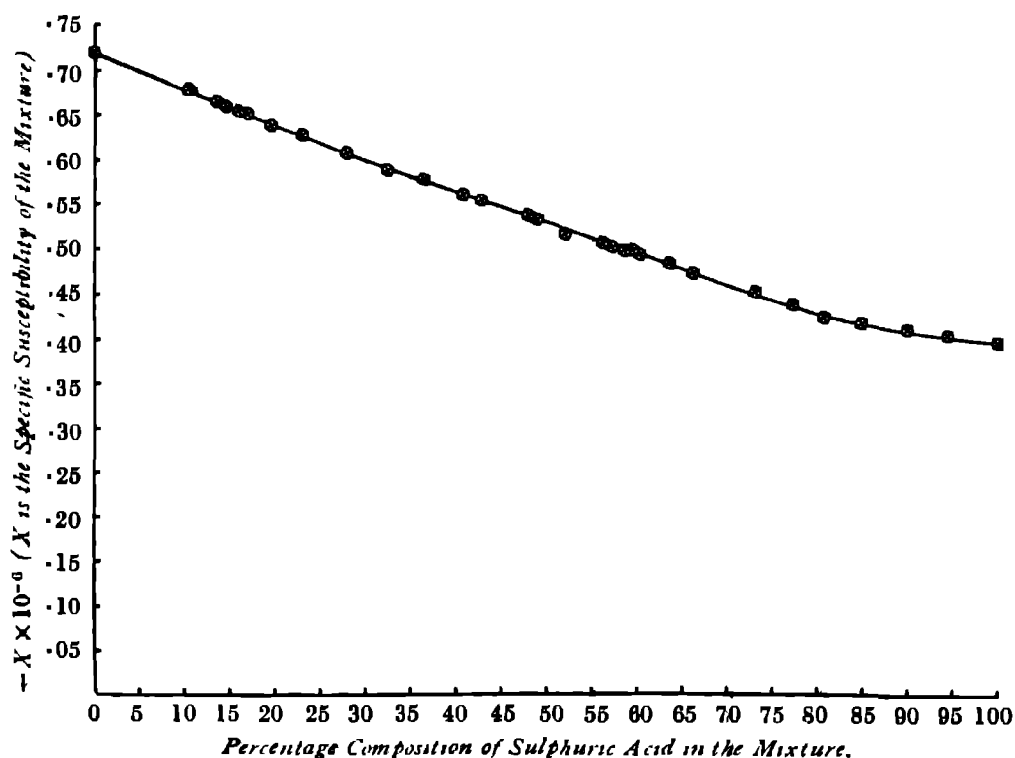
Conc H_2SO_4	X	Conc H_2SO_4	X	Conc. H_2SO_4	X
0%	.720	41.8	.562	74.9	.452
10.3	.680	43.0	.561	78.9	.442
14.1	.664	44.7	.551	78.9	.442
14.3	.664	48.0	.539	78.9	.441
16.5	.657	49.1	.539	82.7	.429
16.7	.654	53.2	.526	86.5	.420
17.5	.653	56.5	.514	91.2	.410
20.5	.641	57.2	.507	92.8	.410
24.4	.625	58.8	.504	92.8	.411
24.7	.625	59.0	.504	93.5	.407
28.1	.611	60.5	.498	95.0	.407
29.2	.610	61.1	.496	96.0	.404
34.4	.591	62.0	.492	96.0	.405
35.3	.585	65.1	.484	97.3	.402
36.5	.580	67.2	.477	98.0	.401
36.5	.580	70.7	.465	99.8	.400
37.6	.579	71.0	.464		

Care is taken to maintain the level of the liquid in the wide tube always the same. The current is adjusted to the same value every time. The deflections were observed by a mirror and scale arrangement. The solutions were prepared in a clean pyrex-glass flask and every time the solution was prepared, it was cooled to the room temperature, before it was poured into the tube. The tube was thoroughly cleaned with the solution before the reading was taken with the solution. The readings tabulated above were obtained in four sets of different concentration. Constantin Salceanu and Dumitru Gheorghiu⁴ and Bhatnagar and Nevgi⁵ have used the same form of instrument and find this instrument most suitable for working with liquids.

Results.

The sulphuric acid was analytically pure and was taken from freshly opened bottles. The densities were determined using a specific-gravity bottle. From a knowledge of the density, the concentration was found from *Landolt and Bornstein Tables*.

The graph shows the value of susceptibility plotted against the percentage concentration of sulphuric acid. The susceptibility of water is assumed to be at 25° C. $\cdot 720 \times 10^{-6}$.



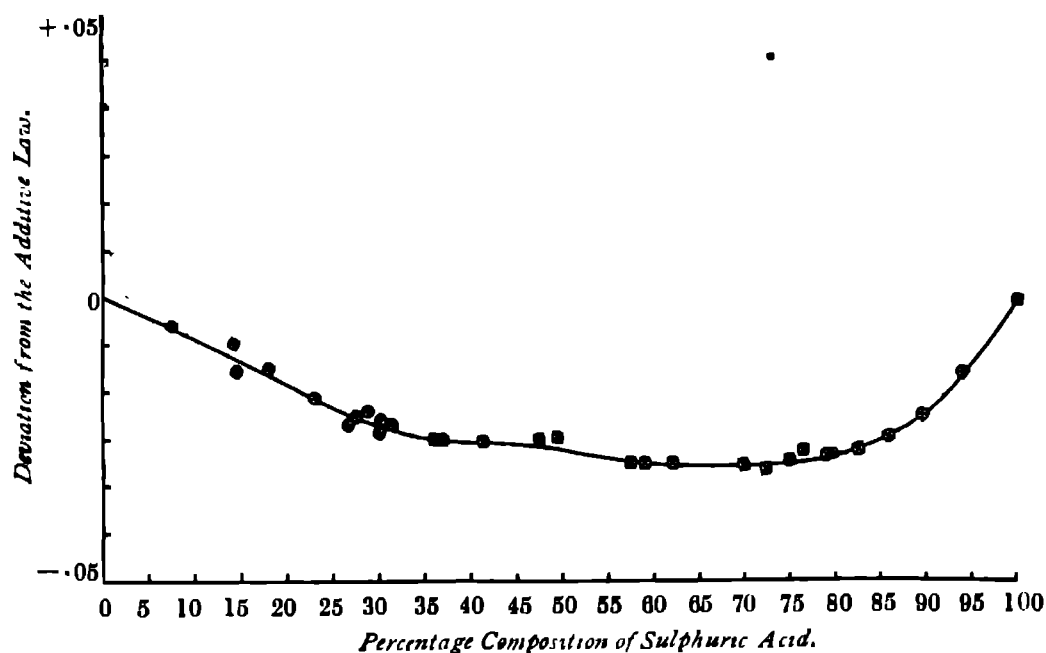
⁴ *Comptes Rendus*, Jan. 7, 1935, 120-123.

⁵ *Ind. Jour. Phys.*, May, 1935.

Discussion.

The graph shows that there is considerable departure from the additive law. The maximum deviation is about 5%. A smooth curve is drawn passing through a maximum number of points and it is seen that most of the points lie on the curve and the points that lie outside the curve differ from the main curve by distances which are within the limits of experimental error. The values are all higher than the additive value, but I find that even above 86% the values are less than the additive value. If the value is taken as $\cdot 400 \times 10^{-6}$, it will be seen that portion of the curve above 86% also lie below the additive straight line joining $\cdot 720$ and $\cdot 400$ and at the same time the maximum deviation from additive law also increases.

The smooth line which has been drawn passing through most of the points shows that there is no definite break anywhere in the concentration susceptibility curve. This shows that the magnetic measurements do not support the theory which assumes the presence of definite hydrates in solution. The deviation from the additive value is plotted against the concentration in the second graph and it is seen that $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ is absent.



The maximum deviation is, however, at a concentration corresponding to the compound $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. This has been reported to be the only compound existing from surface tension data.⁶ Besides $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ can be obtained in a crystalline form.⁷

⁶ *Zeit. f. Phy. Chem.*, 1935, 173, 237.

⁷ *Mellor's Chemistry*.

In conclusion, I wish to record my grateful indebtedness to Prof. B. Venkatesachar for valuable guidance and suggestions. My thanks are due to Mr. Sibaiya for useful discussion and criticism. I am highly thankful to the University of Mysore for the award of a stipend which made this work possible.

ON THE NUMBERS OF WARD AND BERNOULLI.

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(Communicated by Dr. S. Chowla)

§1. INTRODUCTION. Defining $G(n, r)$ as the coefficient of x^{n-r} in the expansion of $(x+1)(x+2)(x+3)\dots(x+n)$, I have shown¹ that

$$G(n+1, r) - G(n, r) = (n+1) G(n, r-1) \quad \dots \quad (1)$$

n and r being integers > 0 .

Defining $G(n, r)$ for all values of n by equation (1), I have shown² that

$$(n-1)! G(-n-1, r) = n^{n+r-1} - \binom{n-1}{1} (n-1)^{n+r-1} \\ + \binom{n-1}{2} (n-2)^{n+r-1} - \dots + (-1)^{n-1} \binom{n-1}{n-1} \cdot 1^{n+r-1} \quad (2)$$

where n and r are integers, $n \geq 1$.

Professor Morgan Ward has shown³ that

$$G(n, r) = \sum_{m=0}^{r-1} \left\{ (-1)^m \cdot H(r, m) \cdot \binom{n+r-m}{2r-m} \right\}, \quad \dots \quad (3)$$

where the H 's are positive integers defined recursively by

$H(r+1, m) = (2r+1-m) \cdot H(r, m) + (r+1-m) \cdot H(r, m-1)$,
with the initial values $H(0, 0) = 1$, $H(r+1, 0) = 1, 3, 5, \dots, (2r+1)$.

Towards the end of his paper, Ward gives expressions for $H(r, r-m)$, $m \leq 5$; with two evident misprints in the last result. Hence he conjectures the form of $H(r, r-m)$. He is, however, not able to prove his statement.

In §2 of this paper, my object is to obtain a definite expression for $H(r, r-m)$. In §3, I study the action of Δ^r on $G(n, r)$. In §4, I obtain an explicit expression for $\sum_{i=1}^n i^r$. This result was of use to me in proving a "Generalisation of Wolstenholme's Theorem"⁴ Finally, I give some expressions for Bernoulli's Numbers in §5.

§2. 1. Professor Ward's H 's and θ 's.

Putting $-m-1$ for n in (3), we get

$$G(-m-1, r) = H(r, r-m) + \binom{r+m}{1} H(r, r-m+1) \\ + \binom{r+m}{2} H(r, r-m+2) + \dots + \binom{r+m}{m-1} H(r, r-1); 1 \leq m \quad \dots (4)$$

Giving to m in succession the values 1, 2, 3, \dots , and making use of (2), we easily obtain all the five results given by Ward. In general, we get

$$H(r, r-m) = \begin{vmatrix} G(-m-1, r), \binom{r+m}{1}, \binom{r+m}{2}, \dots, \binom{r+m}{m-1} \\ G(-m, r), \binom{r+m-1}{0}, \binom{r+m-1}{1}, \dots, \binom{r+m-1}{m-2} \\ G(-m+1, r), 0, \binom{r+m-2}{0}, \dots, \binom{r+m-2}{m-3} \\ \dots, \dots, \dots, \dots, \dots \\ G(-2, r), 0, 0, \dots, \binom{r+1}{0} \end{vmatrix} \quad \dots (5)$$

$$= G(-m-1, r) - \binom{r+m}{1} G(-m, r) + \binom{r+m}{2} G(-m+1, r) - \dots + (-1)^{m-1} \binom{r+m}{m-1} G(-2, r) \dots (6)^*$$

Substituting (6) in (3), we obtain⁵

$$G(n, r) = \sum_{k=1}^r \left\{ (-1)^{r+k} \binom{n+k}{r+k} \binom{n+r+1}{r-k} G(-k-1, r) \right\}.$$

2.2. Multiplying the rows of the determinant in (5) by $(m-1)!, (m-2)!, (m-3)!, \dots, 0!$, in order from top to bottom, and dividing the columns by 1, $(m-2)!, (m-3)!, \dots, 0!$, in order from left to right, we get $(m-1)! H(r, r-m) =$

$$\begin{vmatrix} (m-1)! G(-m-1, r), \binom{m-1}{1} (r+m)^{(1)}, \binom{m-1}{2} (r+m)^{(2)}, \dots, (r+m)^{(m-1)} \\ (m-2)! G(-m, r), \binom{m-2}{0} (r+m-1)^{(0)}, \binom{m-2}{1} (r+m-1)^{(1)}, \dots, (r+m-1)^{(m-2)} \\ (m-3)! G(-m+1, r), 0, \binom{m-3}{0} (r+m-2)^{(0)}, \dots, (r+m-2)^{(m-3)} \\ \dots, \dots, \dots, \dots, \dots \\ 0! G(-2, r), 0, 0, \dots, (r+1)^{(0)} \end{vmatrix}$$

where $j^{(l)}$ denotes as usual $j(j-1)(j-2)\dots(j-l+1)$,

we take $j^{(0)} = 1$ and $0^{(0)} = 1$.

* As a check on the value of $H(r, r-m)$, notice that $H(r, r-m) = 0$, $r = 1, 2, 3, \dots, m-1$; $m \geq 2$.

In view of (2), this determinant can be broken up into m simpler ones. We thus have

$$(m-1)! H(r, r-m) = m^{r+m-1} - \theta_1(r, m) \cdot (m-1)^{r+m-2} \\ + \theta_2(r, m) \cdot (m-2)^{r+m-3} - \dots + (-1)^{m-1} \theta_{m-1}(r, m) \dots (7)$$

where $\theta_k(r, m)$ is a determinant of order $(k+1)$.

2. 3. We now proceed to determine the exact form of $\theta_k(r, m)$
We have

$$\theta_k(r, m) = \begin{vmatrix} \binom{m-1}{k} (m-k)^k & , & \binom{m-1}{1} (r+m)^{(1)} & , & \binom{m-1}{2} (r+m)^{(2)} & , \dots , & \binom{m-1}{k} (r+m)^{(k)} \\ - \binom{m-2}{k-1} (m-k)^{k-1} & , & \binom{m-2}{0} (r+m-1)^{(0)} & , & \binom{m-2}{1} (r+m-1)^{(1)} & , \dots , & \binom{m-2}{k-1} (r+m-1)^{(k-1)} \\ \binom{m-3}{k-2} (m-k)^{k-2} & , & 0 & , & \binom{m-3}{0} (r+m-2)^{(0)} & , \dots , & \binom{m-3}{k-2} (r+m-2)^{(k-2)} \\ \dots & , & \dots & , & \dots & , \dots , & \dots \\ (-1)^k \binom{m-k-1}{0} & , & 0 & , & 0 & , \dots , & \binom{m-k-1}{0} (r+m-k)^{(0)} \end{vmatrix}$$

Multiplying the rows in order from top to bottom, and dividing the columns in order from left to right by

$$1, \frac{(m-1)^{(1)}}{k^{(1)}}, \frac{(m-1)^{(2)}}{k^{(2)}}, \frac{(m-1)^{(3)}}{k^{(3)}}, \dots, \frac{(m-1)^{(k)}}{k^{(k)}};$$

we get

$$\theta_k(r, m) = \binom{m-1}{k} \cdot \begin{vmatrix} (m-k)^k & , & \binom{k}{1} (r+m)^{(1)} & , & \binom{k}{2} (r+m)^{(2)} & , \dots , & (r+m)^{(k)} \\ - (m-k)^{k-1} & , & \binom{k-1}{0} (r+m-1)^{(0)} & , & \binom{k-1}{1} (r+m-1)^{(1)} & , \dots , & (r+m-1)^{(k-1)} \\ (m-k)^{k-2} & , & 0 & , & \binom{k-2}{0} (r+m-2)^{(0)} & , \dots , & (r+m-2)^{(k-2)} \\ \dots & , & \dots & , & \dots & , \dots , & \dots \\ (-1)^k & , & 0 & , & 0 & , \dots , & (r+m-k)^{(0)} \end{vmatrix} \\ = \binom{m-1}{k} \left\{ (m-k)^k + \binom{k}{1} (m-k)^{k-1} (r+m)^{(1)} \right. \\ \left. + \binom{k}{2} (m-k)^{k-2} (r+m)^{(2)} + \dots + \binom{k}{k} (r+m)^{(k)} \right\} \dots (8)$$

In Mathematical short-hand, we may write

$$\theta_k(r, m) \stackrel{b}{=} \binom{m-1}{k} \left\{ (m-k) + (r+m) \right\}^k \dots \dots (8')$$

$\stackrel{b}{=}$ indicating that the powers of $(r+m)$ are to be enclosed within brackets.

Since $k \leq m-1$, it will be readily seen from (8), that $\theta_k(r, m)$ is a polynomial in r of degree k , with positive integral coefficients. This proves Ward's conjecture.

§3. 1. Operations with Δ .

The operator Δ is defined by the relation

$$\Delta \psi(n) = \psi(n+1) - \psi(n).$$

Evidently therefore $\Delta = e^D - 1$, where $D = \frac{d}{dn}$.

Also

$$\begin{aligned} \Delta^j (n-j)^s &= n^s - \binom{s}{1} (n-1)^s + \binom{s}{2} (n-2)^s - \dots \\ &\quad + (-1)^j \binom{s}{j} (n-j)^s \quad \dots \quad (9) \end{aligned}$$

In view of (9), we can write

$$j! G(-j-2, r) = \{\Delta^j n^{r+s}\}_{n=1} \quad , \quad j \geq 0, \quad \dots \quad (2')$$

and $j! G(-j-1, r) = \{\Delta^j n^{r+s}\}_{n=0} \quad , \quad j \geq 1$;

where $\{\}_{n=t}$ indicates that n is to be replaced by t at the end of the operation.

We further have $\Delta^s \hat{n}^{(s)} = s^{(s)} \cdot n^{(s-1)}$, $\dots \dots \dots$ (10)

and

$$\Delta \{f_1(n) \cdot f_2(n)\} = f_1(n) \cdot \Delta f_2(n) + f_2(n+1) \cdot \Delta f_1(n) \quad \dots \quad (11)$$

3. 2. Action of Δ^s on $G(n, r)$.

We have $\Delta G(n, r) = (n+1) G(n, r-1) \quad \dots \dots \dots$ (1')

Repeated application of (11) gives

$$\begin{aligned} \Delta^2 G(n, r) &= (n+1)^2 G(n, r-2) + G(n+1, r-1); \\ \Delta^3 G(n, r) &= (n+1)^3 G(n, r-3) + (3n+5) G(n+1, r-2); \\ \Delta^4 G(n, r) &= (n+1)^4 G(n, r-4) + (6n^2+20n+17) G(n+1, r-3) \\ &\quad + 3 G(n+2, r-2); \end{aligned}$$

In general if $\Delta^s G(n, r)$

$$\begin{aligned} &= f_0(s) \cdot G(n, r-s) + f_1(s) \cdot G(n+1, r-s+1) + \\ &\quad f_2(s) \cdot G(n+2, r-s+2) + \dots + f\left(s, \left[\frac{s}{2}\right]\right) \cdot G\left(n + \left[\frac{s}{2}\right], r-s + \left[\frac{s}{2}\right]\right), \end{aligned} \quad \dots \quad (12)$$

where the f 's are functions of n and s ;

then $\Delta^{s+1} G(n, r) = (n+1) f_0(s) \cdot G(n, r-s-1)$

$$\begin{aligned} &+ \sum_{k=1}^{\left[\frac{s}{2}\right]} \{(n+k+1) f_k(s) + \Delta f_{k-1}(s)\} G(n+k, r-s+k-1) \\ &\quad + \Delta f\left(s, \left[\frac{s}{2}\right]\right) \cdot G\left(n + \left[\frac{s}{2}\right] + 1, r-s + \left[\frac{s}{2}\right]\right). \end{aligned}$$

Hence

$$f_k(s+1) = (n+k+1)f_k(s) + \Delta f_{k-1}(s), \quad 0 \leq k \leq \left[\frac{s}{2} \right] + 1; \quad (13)$$

we take

$$f_{-1}(s) = 0, \text{ also } f_t(s) = 0, \text{ if } t > \left[\frac{s}{2} \right].$$

3. 3. We proceed to obtain an elegant expression for $f_k(s)$.

Since $f_0(s) = (n+1)f_0(s-1)$, and $f_0(1) = (n+1)$;

we have $f_0(s) = (n+1)^s$.

Again

$$f_1(s) - (n+2)f_1(s-1) = \Delta f_0(s-1) = (n+2)^{s-1} - (n+1)^{s-1},$$

$$f_1(s-1) - (n+2)f_1(s-2) = \Delta f_0(s-2) = (n+2)^{s-2} - (n+1)^{s-2},$$

.....

$$f_1(1) - (n+2)f_1(0) = \Delta f_0(0) = (n+2)^0 - (n+1)^0.$$

Multiplying these relations in order by 1, $(n+2)$, $(n+2)^2$, and adding, we get without difficulty

$$\begin{aligned} f_1(s) &= D(n+2)^s - \Delta(n+1)^s, \\ &= \mathcal{D}(n+1)^s; \end{aligned}$$

where \mathcal{D} denotes the operator $De^D - \Delta$ or $(D-1)e^D + 1$

Proceeding as above, we get without much difficulty,

$$2! f_2(s) = \mathcal{D}^2(n+1)^s.$$

This suggests the form for $f_k(s)$ We have in fact

$$k! f_k(s) = \mathcal{D}^k(n+1)^s \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

We have simply to show that (14) satisfies (13).

It is well known that

$$\phi(D) n^{s+1} - n \phi(D) n^s = \phi'(D) n^s,$$

where $\phi'(D) = \frac{d}{dD} \phi(D)$.

It follows that

$$\begin{aligned} f_k(s+1) - (n+k+1)f_k(s) &= \frac{1}{k!} \left\{ \mathcal{D}^k(n+1)^{s+1} - (n+1) \mathcal{D}^k(n+1)^s - k \mathcal{D}^k(n+1)^s \right\}, \\ &= \frac{1}{k!} \left\{ \frac{d}{dD} \mathcal{D}^k - k \mathcal{D}^k \right\} (n+1)^s, \\ &= \frac{1}{(k-1)!} \left\{ De^D - \mathcal{D} \right\} \mathcal{D}^{k-1}(n+1)^s, \\ &= \frac{1}{(k-1)!} \Delta \mathcal{D}^{k-1}(n+1)^s = \Delta f_{k-1}(s). \end{aligned}$$

Now, (14) is easily established by inductive reasoning.

Since $D = (D-1) e^0 + 1$,

$$= \frac{D^0}{2!} + \frac{2 D^0}{3!} + \frac{3 D^0}{4!} + \dots + \frac{(j-1) D^j}{j!} + \dots$$

so $f_k(s)$ is of degree $s-2k$ in n .

In particular, $f_k(2k) = \frac{(2k)!}{k! 2^k}$, a constant ;

$$f_k(2k+1) = \frac{(2k+1)!}{k! 2^k \cdot 3} \{3n+3+2k\} ;$$

and $f_k(s) = 0$ when $k > \left\lceil \frac{s}{2} \right\rceil$.

§4. 1. To prove that for all positive integral values of s ,

$$n^s = n^{(s)} + G(-s, 1) \cdot n^{(s-1)} + G(-s+1, 2) \cdot n^{(s-2)} + \dots + G(-2, s-1) \cdot n^{(1)}.$$

Let $n^s = \sum_{j=1}^s c_j n^{(j)}$, where the c_j 's are functions of s .

Then, we have $j! G(-j-1, s-j) = \{\Delta^j n^s\}_{n=0}$, $j \geq 1$.

$$\begin{aligned} &= \left\{ \Delta^j \sum_{i=1}^s c_i n^{(i)} \right\}_{n=0}, \\ &= \left\{ \sum_{i=1}^s c_i (i)^{(j)} \cdot n^{(i-j)} \right\}_{n=0}, \\ &= c_j \cdot j^{(j)} = j! c_j. \end{aligned}$$

whence $c_j = G(-j-1, s-j)$,

$$\text{and } n^s = \sum_{j=1}^s \{G(-j-1, s-j) \cdot n^{(j)}\} \quad \dots \quad (15)$$

4.2 From (15), we readily obtain

$$\sum_{i=1}^n i^s = \sum_{j=1}^s \left\{ G(-j-1, s-j) \cdot \frac{(n+1)^{(j+1)}}{j+1} \right\}, \quad s > 0. \quad \dots \quad (16)$$

Since $(n+1)^{(j+1)} = n^{(j+1)} + (j+1) n^{(j)}$,

and $G(-j, s-j+1) + j \cdot G(-j-1, s-j) = G(-j-1, s-j+1)$,

therefore $\sum_{i=1}^n i^s = \sum_{j=1}^{s+1} \left\{ G(-j-1, s-j+1) \cdot \frac{n^{(j)}}{j} \right\}, \quad s \geq 1. \quad \dots \quad (17)$

In particular, we get

$$\begin{aligned} \sum_{i=1}^n i^3 &= G(-2, 2) \cdot \frac{(n+1)^{(3)}}{2} + G(-3, 1) \cdot \frac{(n+1)^{(3)}}{3} + G(-4, 0) \cdot \frac{(n+1)^{(4)}}{4}, \\ &= \frac{(n+1)^{(2)}}{2} + 3 \cdot \frac{(n+1)^{(3)}}{3} + \frac{(n+1)^{(4)}}{4} = \left\{ \frac{n(n+1)}{2} \right\}^2. \end{aligned}$$

§5. Bernoulli's Numbers.

It is well known that

$$\sum_{i=1}^n i^s = \frac{n^{s+1}}{s+1} + \left\{ \frac{1}{2} + \frac{B_2}{2!} D + \frac{B_4}{4!} D^3 + \frac{B_6}{6!} D^5 + \dots + \frac{B_2 \left[\frac{s}{2} \right]}{(2 \left[\frac{s}{2} \right])!} D^2 \left[\frac{s}{2} \right]^{-1} \right\} n^s \quad \dots (18)$$

where the B's are Bernoulli's numbers.

Putting $s = 2t$ and equating the coefficients of n in (16), (17) and (18), we get

$$B_{2t} = G(-2, 2t) - \frac{1!}{2} G(-3, 2t-1) + \frac{2!}{3} G(-4, 2t-2) - \dots + \frac{(2t)!}{2t+1} \quad \dots (19)$$

$$= \frac{0!}{2} G(-2, 2t-1) - \frac{1!}{3} G(-3, 2t-2) + \frac{2!}{4} G(-4, 2t-3) - \dots - \frac{(2t-1)!}{2t+1} \quad \dots (19')$$

Again putting $s = 2t + 1$, we obtain in the same manner,

$$0 = G(-2, 2t+1) - \frac{1!}{2} G(-3, 2t) + \frac{2!}{3} G(-4, 2t-1) - \dots - \frac{(2t+1)!}{2t+2} \quad \dots (20)$$

$$= \frac{0!}{2} G(-2, 2t) - \frac{1!}{3} G(-3, 2t-1) + \frac{2!}{4} G(-4, 2t-2) - \dots + \frac{(2t)!}{2t+2} \quad \dots (20')$$

These results are easily verified.

§6. To prove that for all positive integral values of $r > 0$,

$$G(-2, r) - 1! G(-3, r-1) + 2! G(-4, r-2) - \dots + (-1)^{r-1} r! G(-r-2, 0) = 0.$$

We have $j! G(-j-2, r) = \{\Delta^j n^{r+r}\}_{n=1}$.

$$\text{Now, } \sum_{j=0}^r \{(-1)^j \cdot j! G(-j-2, r-j)\}$$

$$= \sum_{j=0}^r \{(-1)^j \cdot \Delta^j n^r\}_{n=1},$$

$$= \{(1 - \Delta + \Delta^2 - \dots + (-1)^r \Delta^r) n^r\}_{n=1},$$

$$= \left\{ \frac{1}{1 + \Delta} n^r \right\}_{n=1}; \text{ for } \Delta^s n^r = 0, \quad s > r;$$

$$= \{(n-1)^r\}_{n=1} = 0, \quad \text{since } r \geq 1;$$

and so the proposition is proved.

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POLARISATION OF THE RAMAN BANDS OF WATER AND DEUTERIUM OXIDE.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

1 Introduction

IN two previous communications¹ the author has reported the results of a study of the Raman spectrum of heavy water, and has pointed out the remarkable similarity in the structure and relative intensity of the Raman bands of this substance and those of ordinary water. In order to complete this investigation, it was felt desirable to study the state of polarisation of the Raman bands in the two cases. Results obtained in this direction are communicated in the present paper.

The polarisation of the Raman bands of ordinary water has been studied by Ramaswamy,² Cabannes and Rousset,³ Cabannes and De Riols⁴ and Ramakrishna Rao.⁵ The results of the different authors are rather conflicting. Ramaswamy found the values 0.6, 0.45 and 0.75 for the depolarisation of the three components of the principal Raman band in the order of increasing frequency. Cabannes and Rousset reported the first component as depolarised and the second one as polarised. Cabannes and De Riols reported quite the contrary result. They found that all the three components are polarised. They gave 0.3 as the depolarisation factor for the central component and remarked that the one of lower frequency is still more polarised. Ramakrishna Rao used a quartz spectrograph in his experiments and got highly anomalous results.

2 Experimental

The liquids (H_2O and D_2O) rendered dust-free by vacuum distillation were contained in suitable Raman tubes of pyrex glass with fused-on end

¹ R. Ananthakrishnan, *Nature*, 1935, **136**, 551

R. Ananthakrishnan, *Proc. Ind. Acad. Sci. (A)*, 1935, **2**, 291.

² C. Ramaswamy, *Nature*, 1931, **127**, 558.

³ J. Cabannes and A. Rousset, *Ann. de Phys.*, 1933, **19**, 271.

⁴ J. Cabannes and J. De Riols, *C. R.*, 1934, **198**, 30

⁵ I. R. Rao, *Z. f. Phys.*, 1935, **90**, 658

window. The experimental tube was kept at a distance of about 50 cms. from the slit of the spectrograph and light from a 6-inch quartz mercury lamp was concentrated on it by means of a large glass condenser. The observation window was a circular aperture of 3 mms. diameter. A quartz double image prism with its axes horizontal and vertical was interposed between the slit and the Raman tube and fixed in such a position that the two images of the aperture as viewed through the prism could be seen well separated one above the other. A lens behind the double image prism focussed the two images on the slit of the spectrograph (Hilger two-prism glass optical parts). The time of exposure to get an intense picture was about 2 days in the case of water and 4 days in the case of deuterium oxide using a slit width of $75\ \mu$.

3 Results.

The spectra photographed in the above manner are reproduced in the plate. The principal results may be summarised as follows:

(1) The three components of the principal Raman bands of H_2O and D_2O are more and more depolarised in the order of increasing frequency shift. The component of lowest frequency shows a high degree of polarisation, the depolarisation factor being probably of the order of 10 or 15%. The component of highest frequency is highly depolarised, perhaps to the limiting value $6/7$. The middle component which is the strongest has a depolarisation factor somewhere between these two values, about 40–50%.

(2) The band $\Delta\nu = 1235\ \text{cm}^{-1}$ in the case of D_2O is depolarised to the extent of 50–60%. The depolarisation of the corresponding Raman band in the case of H_2O ($\Delta\nu = 1650\ \text{cm}^{-1}$) could not be ascertained because of its unfavourable position in the spectrum. Cabannes and De Riols have found for it the value $\rho \approx 0.4$.

(3) The band $\Delta\nu = 175\ \text{cm}^{-1}$ which is quite strong with pronounced anti-stokes is depolarised to the limiting extent of $6/7$ in both cases.

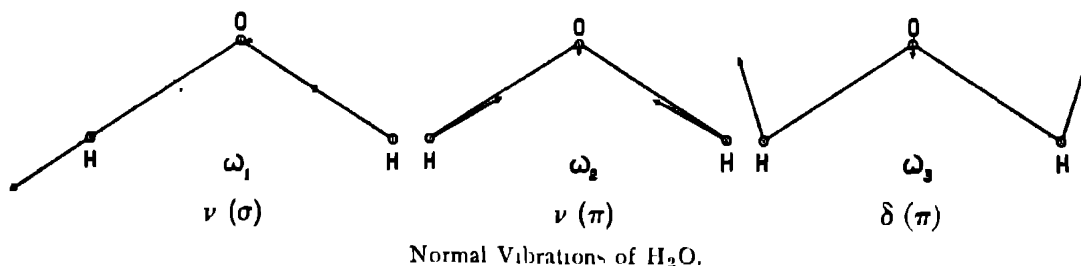
(4) The diffuse bands $\Delta\nu = 500\ \text{cm}^{-1}$ and $\Delta\nu = 750\ \text{cm}^{-1}$ in the case of H_2O seem to be highly depolarised. The corresponding Raman bands $\Delta\nu = 350\ \text{cm}^{-1}$ and $\Delta\nu \approx 500\ \text{cm}^{-1}$ recently reported by Magat^a in the case of D_2O are hardly perceptible in the author's photographs.

4. Discussion of Results

A strict and satisfactory interpretation of the Raman spectra of liquid H_2O and D_2O appears to be very difficult indeed. Nevertheless, there have been certain attempts in this direction, although only of an empirical nature.

^a M. Magat, *C. R.*, 1935, 201, 668.

Mecke's analysis of the vibration-rotation spectrum of ordinary water vapour led him to the choice of the following normal frequencies for the H_2O



molecule in the vapour state. $\nu(\sigma) = \omega_1 = 3795 \text{ cm}^{-1}$; $\nu(\pi) = \omega_2 = 3670 \text{ cm}^{-1}$; $\delta(\pi) = \omega_3 = 1615 \text{ cm}^{-1}$. These may be compared with the infra-red absorption maxima at 3756 and 1595 and the Raman line at 3654 cm^{-1} observed in the Raman spectrum of water vapour.

The infra-red absorption spectra of liquid H_2O and D_2O have been studied recently by Ellis and Sorge.⁷ They have identified the absorption maxima at 6.2μ (1613 cm^{-1}) and 3μ (3330 cm^{-1}) in the case of liquid water with the fundamental frequencies assigned by Mecke to the H_2O molecule. The shift in the absorption maxima from the gaseous state to the liquid state is not surprising when it is remembered that many of the molecules contributing to these bands are parts of polymer molecules. Ellis and Sorge have also pointed out that more detailed information about the 3μ absorption region is to be sought for from the Raman spectrum which yields three components, the average of the maxima being approximately 3220 , 3430 , and 3600 cm^{-1} . The effect of temperature on the 3μ Raman band of water is to diminish the intensity of the component of lowest frequency and increase the intensity of the component with the highest frequency. This is explained as being due to breaking up of the polymerised molecules. Ellis and Sorge have therefore chosen the Raman bands at 3430 and 3600 to correspond to the vibrational modes $\nu(\pi)$ and $\nu(\sigma)$ respectively for the H_2O molecules in the liquid state. Magat⁸ on the other hand has suggested that in so far as the component of frequency 3600 is extremely weak if not entirely absent at low temperatures and increases in intensity as the temperature is raised, it should be identified with the Raman line 3654 of water vapour and arises from a small percentage of water molecules which possess free rotation. The two other components 3220 and 3430 which are quite intense at ordinary temperature represent according to him the fundamental frequencies $\nu(\pi)$ and $\nu(\sigma)$ of the liquid molecules. Ramakrishna Rao's suggestion that the

⁷ J. W. Ellis and B. W. Sorge, *Jour. Chem. Phys.*, 1934, 2, 559.

⁸ M. Magat, *Bull. de la Soc. de Phys.*, 1935, 60, 65.

M. Magat, *C.R.*, 1935, 201, 669.

component bands at 3220, 3430, and 3600 ought to be attributed respectively to the molecules $(\text{H}_2\text{O})_3$, $(\text{H}_2\text{O})_2$, and H_2O is only conjectural.

In order to interpret at least in a qualitative fashion the polarisation results, it might be pointed out that the polarisation rules in Raman scattering give the depolarisation factor $6/7$ for anti-symmetrical and degenerate modes, and values between 0 and $6/7$ for symmetrical vibrations. Thus in the case of H_2O and D_2O , the Raman band corresponding to $\nu(\sigma)$ would be highly depolarised, while those corresponding to $\nu(\pi)$ and $\delta(\pi)$ would show a lesser degree of depolarisation. It is also reasonable to conclude that $\delta(\pi)$ would be much more depolarised than $\nu(\pi)$.

The high depolarisation of the Raman band at 3600 renders it difficult to identify it with the vapour frequency 3654 which presumably corresponds to $\nu(\pi)$. Rather, it supports the view of Ellis and Sorge that it arises from the anti-symmetrical vibration of the liquid molecules. The high degree of polarisation of the component band at 3220 on the other hand suggests that it should arise from a symmetrical vibration.

It appears that the influence of temperature as well as the observed polarisation results could be satisfactorily explained if we postulate that the liquid state is composed of a large percentage of polymerised molecules (di-hydrol) and a smaller percentage of non-polymerised molecules. To the former belong the vibrational frequencies $\nu(\pi) = 3220$ and $\nu(\sigma) = 3430$ while to the latter belong the frequencies $\nu(\pi) = 3430$ and $\nu(\sigma) = 3600$. This assumption will naturally explain the intermediate degree of depolarisation observed for the central component since it is now a superposition of the depolarised anti-symmetrical vibration of the polymerised and the symmetrical vibration of the non-polymerised molecules. The observation of Magat that the intensity maximum displaces itself in the direction of increasing frequency in the two stronger components as the temperature is raised is also not difficult to understand on this assumption since the coupling between two molecules is bound to be influenced by forces of thermal agitation.

If the view suggested above is correct, the same considerations should explain the Raman spectrum of heavy water as well. The vibrational frequencies of the liquid D_2O molecules appear in the Raman spectrum as a sharp band at 1235 cm^{-1} and a broad and intense band at 2500 cm^{-1} . The latter band shows a structure exactly analogous to the corresponding Raman band of ordinary water, with two strong components at 2360 and 2510 and a fainter one at 2660. Polarisation photographs show quite analogous features.



Polarisation of Paman Bands

(a) D_2O (n) H_2O

The infra-red spectrum of the liquid investigated by Ellis and Sorge led them to the choice of the absorption bands at 8.2μ (1220 cm^{-1}) and 4μ (2500 cm^{-1}) as corresponding to the fundamental frequencies. The fundamental vapour frequencies in the infra-red observed by Barker and Sleator⁹ and by Bartholomé and Clusius¹⁰ are 2775 and 1185, while Rank, Larsen and Bordner¹¹ found a single Raman line at 2666 cm^{-1} for the vapour which presumably arises from the symmetric vibration

The origin of the strong low frequency Raman band at 175 cm^{-1} has been diversely interpreted. The strong infra-red absorption in practically the same region as well as the high depolarisation exhibited by this Raman band, would seem to favour the view that it arises from the hindered rotation or angular oscillation of the liquid molecules. Magat's suggestion¹² that this band owes its origin to the mutual oscillation of the centres of gravity of two liquid molecules without change of orientation cannot explain the high depolarisation observed for this band.

In conclusion, the author wishes to record his respectful thanks to Professor Sir C. V. Raman for his kind interest and guidance in the present work

5. Summary

The Raman spectra of liquid H_2O and D_2O have been photographed by interposing a double image prism in front of the slit of the spectrograph. The three components of the principal Raman band in the two cases are more and more depolarised in the order of increasing frequency, the component of lowest frequency being highly polarised, and that of highest frequency being highly depolarised. The band $\Delta\nu = 1235\text{ cm}^{-1}$ in the case of D_2O is imperfectly polarised, while the low frequency Raman band ($\Delta\nu \approx 175\text{ cm}^{-1}$) is depolarised to the extent of 6/7 in both cases. A tentative explanation is suggested to interpret the observed results

⁹ E. F. Barker and W. W. Sleator, *Jour. Chem. Phys.*, 1935, **3**, 660.

¹⁰ E. Bartholomé and K. Clusius, *Naturwiss.*, 1934, **22**, 40; *Z. f. Elek. Chem.*, 1934, **40**, 530.

¹¹ D. H. Rank, K. D. Larsen and E. R. Bordner, *Jour. Chem. Phys.*, 1934, **2**, 464.

¹² M. Magat, *loc. cit.*

ANTISEPTICS AND ANTHELMINTHICS.

Part II. A Synthesis of 6-Benzyl-7-hydroxyflavone and 6-*n*-Hexyl-7-hydroxyflavone.

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IN view of the therapeutic value of hexylresorcinol¹ as an internal antiseptic² extensive work on the alkyl derivatives of other phenols has been reported.³

Since the anthelmintic constituent of the leaves of *Calycopteris floribunda* has been identified as a dihydroxytetramethoxyflavone⁴ the examination of Indian plants with alleged vermifugal action for the presence of flavone derivatives, and of synthetic specimens of the latter for anthelmintic properties, has become relevant to the general attempt to prepare new antiseptics and anthelmintics.⁵ Nakao and Tseng⁶ have isolated apigenin and its 7-methyl ether from the Chinese drug "Yuen-hua", believed from very early times to be a diuretic and anthelmintic, but the pharmacological action has not been correlated with the flavone content. The present work relates to the synthesis of the 6-benzyl and hexyl derivatives of 7-hydroxyflavone. The influence of a C-benzyl group on the bactericidal action of phenols and halogenated phenols has been demonstrated by Klarman, Gates and Shternov.⁷

4-Benzylresorcinol (2 : 4-dihydroxydiphenylmethane) was prepared according to Klarman⁸, the homogeneity of the product and the absence of

¹ Johnson and Lane, *J. Amer. Chem. Soc.*, 1921, **43**, 348.

² Leonard and others, *J. Amer. Med. Assoc.*, 1924, **83**, 2005, *et sequa*.

³ Dohme, Cox and Miller, *J. Amer. Chem. Soc.*, 1926, **48**, 1688; Klarman and Woweru, *J. Amer. Chem. Soc.*, 1929, **51**, 605; Brewster and Harris, *J. Amer. Chem. Soc.*, 1930, **52**, 4866; Coulthard, Marshall and Pym, *J. Chem. Soc.*, 1930, **137**, 280, Klarman, *Soap*, 1932, **8**, 99; 1934, **10**, 87; etc.

⁴ Ratnagiriswaran, Sehra and Venkataraman, *Biochem. Jour.*, 1934, **28**, 1964.

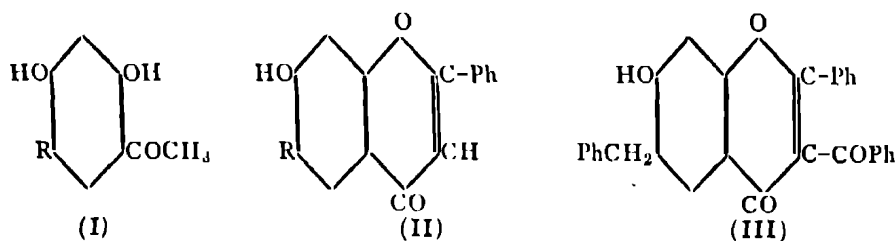
⁵ Gulati, Seth and Venkataraman, *Jour. pr. Chem.*, 1933, **137**, 47.

⁶ *Jour. Pharm. Soc. Japan*, 1932, No. **602**, 343; 1933, No. **608**, 905.

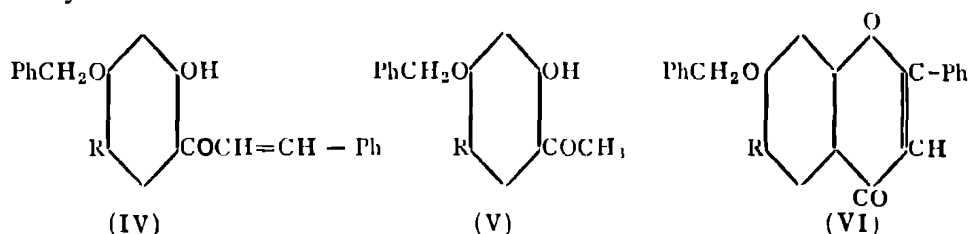
⁷ *J. Amer. Chem. Soc.*, 1932, **54**, 3315.

⁸ *J. Amer. Chem. Soc.*, 1926, **48**, 791.

2 : 4-dibenzylresorcinol were confirmed by comparison with the product of the Clemmensen reduction of resobenzophenone. The phenol was then converted into 5-benzylresacetophenone (I ; R = CH₂Ph) by a Hoesch reaction with acetonitrile. Treatment of the ketone with benzoic anhydride led to a mixture of 6-benzyl-7-hydroxyflavone (II ; R = CH₂Ph) and



its 3-benzoyl derivative (III), the former being also prepared by the selenium dioxide oxidation of the chalcone (IV; $R = CH_2Ph$), followed by debenzoylation



By analogy with the Fries reaction on 7-acyloxycoumarins and chromones,⁹ which give rise to 8-substituted products, the Claisen change of 7-benzoyloxyflavone was studied with the object of preparing 7-hydroxy-8-benzoylflavone, but attempts at migration with zinc chloride or aluminium chloride resulted only in unchanged material or debenzylation to 7-hydroxyflavone. Difficulties were also encountered in efforts to prepare 7-hydroxy-8-benzoylflavone and reduce it to the desired substance.

By submitting 4-*n*-hexylresorcinol to the series of reactions outlined in the case of 4-benzylresorcinol, the ketone (I; R = *n*-hexyl), the chalkone (IV; R = *n*-hexyl) and the flavone (II; R = *n*-hexyl) were prepared.

Experimental.

C-Benzylresorcinol —(a) Prepared according to Klaimann (*loc. cit.*) the substance was obtained in a yield of 35 %, the oil distilling at 198–200°/2 mms. The colourless needles from petroleum ether melted at 76–77°. (b) A mixture of resorcinol (25 g.), benzyl chloride (7.5 g.) and fused zinc chloride (2 g.) was warmed carefully on the water-bath until a vigorous reaction set in. More benzyl chloride (7.5 g.) was then added, the whole being finally heated for one hour on the water-bath. On cooling, water was added, the mixture

⁹ Limaye, *Ber.*, 1934, 67, 12; Wittig, Baugert and Richter, *Ann.*, 1925, 446, 184.

extracted with ether, the ether extract washed with 2% sodium carbonate solution, dried and the solvent removed. Distillation of the residue *in vacuo* gave 15 g. of an oil boiling at 210-220°/12-13 mms., which was redistilled and collected at 198-200°/2 mms. (8 g.). (c) Resobenzophenone (20 g.), zinc amalgam (86 g.), aldehyde-free alcohol (60 g.) and 50% hydrochloric acid (140 g.) were boiled for 30 hours, when a drop of the oily product, taken up in alcohol and carefully neutralised, gave no colouration with ferric chloride. Ether extraction and distillation at 2 mms. pressure gave C-benzylresorcinol in 50% yield.

C-Benzylresacetophenone (I; R = CH₂Ph).—After saturation of a mixture of C-benzylresorcinol (10 g.), acetonitrile (3.5 c.c.), ether (30 c.c.) and zinc chloride (4 g.) with hydrogen chloride, and 4 days in the ice-chest, the ether was decanted off, the residue boiled with water (250 c.c.) and filtered hot. The undissolved oil solidified on cooling and crystallised from benzene in very pale yellow leaflets (6 g.), m.p. 153° (Found: C, 74.1; H, 5.7. C₁₈H₁₄O₃ requires C, 74.4; H, 5.8%). The alcoholic solution exhibited a deep violet colouration with ferric chloride. The *dinitrophenylhydrazone* melted at 221° (Found: N, 13.0. C₂₁H₁₈O₆N₄ requires N, 13.3%). When the reaction was carried out with an impure C-benzylresorcinol, b.p. 210-220°/10-12 mms., the hot aqueous filtrate after removal of C-benzylresacetophenone, deposited colourless leaflets (0.4 g.) on cooling, which melted at 209° and gave an orange-red ferric chloride colouration (Found: C, 75.0; H, 5.9).

2-Hydroxy-4-benzyloxy-5-benzylacetophenone (V; R = CH₂Ph).—Benzylation in the known manner¹⁰ gave the ether, which crystallised from alcohol in colourless needles, m.p. 111° (Found: C, 79.4; H, 6.0. C₂₂H₂₀O₃ requires C, 79.5; H, 6.0%). The colour with ferric chloride was deep red.

2-Hydroxy-4-benzyloxy-5-benzylchalkone (IV; R = CH₂Ph).—To a warm solution of the above ketone (2.3 g.) and benzaldehyde (1.3 g.), 50% caustic soda solution (6 g.) was added. On leaving overnight, the chalkone was isolated as usual. The deep yellow needles (2.3 g.) from glacial acetic acid melted at 134° (Found: C, 82.8; H, 6.2. C₂₀H₂₄O₃ requires C, 82.9; H, 5.7%). The crystals were coloured orange-red by sulphuric acid.

6-Benzyl-7-benzyloxyflavone (VI; R = CH₂Ph).—From a mixture of the above chalkone (2 g.), selenium dioxide (2 g.) and amyl alcohol (12 c.c.), refluxed at 150° for 12 hours, the solvent was removed in steam, and the residue extracted with glacial acetic acid. The colourless needles (1 g.) separating from the filtrate melted at 222° (Found: C, 83.0; H, 5.4.

¹⁰ Gulati, Seth and Venkataraman, *J. Chem. Soc.*, 1934, 1766.

$C_{20}H_{22}O_3$ requires C, 83.2 ; H, 5.3 %). The colourless solution in sulphuric acid exhibited a blue fluorescence.

6-Benzyl-7-hydroxyflavone (II ; $R = CH_2Ph$)—To the benzyl ether (1 g) in glacial acetic acid (10 c.c.), hydrobromic acid saturated at 0° (10 g.) was added and the solution refluxed for an hour. Dilution with water and crystallisation of the precipitate from glacial acetic acid gave cream-coloured, elongated, triangular plates, m.p. 267° (Found : C, 80.6 ; H, 5.0. $C_{22}H_{16}O_3$ requires C, 80.5 ; H, 4.9 %). The *acetyl* derivative, colourless needles from alcohol, melted at 191° (Found : C, 78.1 ; H, 4.9. $C_{24}H_{18}O_4$ requires C, 77.8 ; H, 4.8 %).

3-Benzoyl-6-benzyl-7-hydroxyflavone (III).—The Robinson reaction with C-benzylresacetophenone (4 g), benzoic anhydride (40 g.) and sodium benzoate (8 g.), hydrolysis with 10% alcoholic potash (210 c.c.) and saturation with carbon dioxide led to a yellow powder, crystallisation of which from glacial acetic acid gave colourless plates (1.5 g.), m.p. 267° , identical with the previously obtained flavone. Concentration of the mother-liquors and dilution gave thin, colourless plates, m.p. 229° (Found : C, 80.2 ; H, 4.6. $C_{28}H_{20}O_4$ requires C, 80.6 ; H, 4.6 %).

C-Hexylresacetophenone (I ; $R = n\text{-hexyl}$)—The product, obtained by the Hoesch reaction between hexylresorcinol¹¹ (30 g) acetonitrile (12 g) and zinc chloride (12 g.) in ether (50 c.c.), followed by aqueous hydrolysis, was an oil, which was taken up in ether. After removal of the ether from the dried extract and distillation of the residue *in vacuo*, the fraction coming over at $195\text{--}200^\circ/3\text{--}4$ mms. solidified in contact with light petroleum. The colourless plates (24 g.) from the same solvent melted at 85° (Found : C, 71.1 ; H, 8.7. $C_{14}H_{20}O_3$ requires C, 71.2 ; H, 8.5 %). The ferric chloride colouration was deep red. The *dinitrophenylhydrazones* melted at $183\text{--}184^\circ$ (Found : N, 13.3. $C_{20}H_{24}O_6N_4$ requires N, 13.4 %).

2-Hydroxy-4-benzoyloxy-5-hexylacetophenone (V ; $R = n\text{-hexyl}$).—The colourless needles from alcohol melted at 94° (Found : C, 77.6 ; H, 8.2. $C_{21}H_{26}O_3$ requires C, 77.3, H, 8.0 %).

2-Hydroxy-4-benzoyloxy-5-hexylchalcone (IV ; $R = n\text{-hexyl}$)—Yellow needles from alcohol, m.p. 92° (Found : C, 81.3 ; H, 7.4. $C_{28}H_{30}O_3$ requires C, 81.1 ; H, 7.2 %). The alcoholic solution turned dark brown with ferric chloride.

6-Hexyl-7-benzoyloxyflavone (VI ; $R = n\text{-hexyl}$).—The oxidation of the chalcone (16 g.) with selenium dioxide (18 g.) resulted in an oil, which

¹¹ Dohme, Cox and Miller, *Jour. Amer. Chem. Soc.*, 1926, **48**, 1688.

solidified on cooling, and the colourless needles (4 g.) from glacial acetic acid melted at 120° (Found : C, 81.5 ; H, 6.9. $C_{28}H_{28}O_3$ requires C, 81.5 ; H, 6.7 %).

6-Hexyl-7-hydroxyflavone (II ; R = *n*-hexyl).—Colourless needles from alcohol, m p. $191-192^{\circ}$ (Found : C, 78.5 ; H, 6.9 $C_{21}H_{22}O_3$ requires C, 78.3 ; H, 6.8 %) The alcoholic solution was unchanged in colour by the addition of ferric chloride and the colourless solution in sulphuric acid showed a blue fluorescence. The *acetyl* derivative, colourless needles from alcohol, melted at 104° (Found : C, 75.5 ; H, 6.6 $C_{23}H_{24}O_4$ requires C, 75.8 ; H, 6.6 %).

SCATTERING OF LIGHT IN OPTICAL GLASSES.

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(Communicated by Sir C. V. Raman, Kt., FRS, N L)

1. Introduction.

THE constitution and structure of glass have long been a puzzling problem. It is, nevertheless, true to say that there has been comparatively little work done of a fundamental or theoretical nature. This is no doubt due to the meagre knowledge we possess concerning the constitution of glass. It is obvious that glasses do not consist of crystallites which can be recognised as such by the naked eye even when assisted by powerful microscopes. Glasses are usually described as supercooled liquid or as an amorphous solid; the word amorphous as used by the workers on glass is taken to mean that no crystallites can be detected by the ordinary laboratory methods. From its state of aggregation one is led to believe that glass is a supercooled liquid for it exhibits a series of thermodynamic characteristics of such a condition. Data on specific heat, surface tension, melting point, viscosity and dielectric strength indicate that the material is of high molecular weight or highly associated. But on the other hand as regards its elastic properties, glass behaves more or less like a hard rigid solid.

X-ray diffraction by glasses has been studied in detail by numerous investigators beginning with Debye and Scherrer. The lack of obvious crystallinity makes it clear that sharp diffraction patterns are unlikely to be obtained. Most glasses exhibit broad and diffuse bands similar to those obtained in the case of ordinary liquids. Randall and Rooksby¹ tried to explain the different bands on the basis of minute crystals or groups of atoms regularly arranged over a very small volume. But such a view regarding the constitution of glass does not find support from other directions.

It has long ago been pointed by Prof. Raman² that a study of the scattering of light in glasses would enhance our knowledge regarding the nature of glass and amorphous substances in general, to a considerable extent. The present

¹ J. T. Randall and H. P. Rooksby, *Journ. Soc. Glas. Techn.*, 1933, 17, 287.

² C. V. Raman, *Molecular Diffraction of Light*, 1922.

Lord Rayleigh³ was the first to demonstrate the existence of an internal scattering of light in common glasses. The degree of depolarisation was found to be of the same order of magnitude as that usually observed in gases. He was inclined to attribute the scattering in glasses to spherical inclusions of diameter not small compared with the wavelength of light and explained the finite depolarisation of the scattered light as due to the appreciable size of these inclusions. It is well known that opal glasses owe their diffusing properties to the fact that they contain in suspension small crystals which can be observed under an ordinary microscope, of refractive index and absorption coefficient different from those of the glassy matrix. But it is hard to believe that such inclusions may also exist in optical glasses. Prof. Raman⁴ has reported the measurements of intensity and depolarisation of light scattered by a series of optical glasses. The closest examination by him under a powerful microscope with dark ground illumination failed to indicate the presence of any visible inclusions. Consequently he came to the conclusion that the scattering in these glasses was really molecular in origin. He found that the scattering power of glass approximated to that of a liquid and not to that of a crystal.

The observations of the above-mentioned investigators on the scattering of light in glass did not carry us far into the more intricate problem concerning the constitution of glass, for they studied the Rayleigh radiation with incident unpolarised light alone. In order to get more comprehensive and fundamental information regarding the state of aggregation or dispersion of molecules in any scattering medium, it is essential to make a comparative study of the state of polarisation of the scattered light with the incident light in different states of polarisation, (namely, unpolarised, vertically polarised and horizontally polarised). This fact has often been stressed by the author in recent papers⁵ in these *Proceedings*. If glass is an aggregate of molecular clusters, the light scattered transversely when the incident light is polarised with electric vector horizontal, will no longer be completely unpolarised as in the case of an ordinary liquid or gas but will be partially polarised with the horizontal component stronger than the vertical component to an extent depending upon the size of the clusters present. The object of the present investigation is to make a more detailed study of the scattering of light in a series of optical glasses of widely different composition and to discuss the bearing of the results on the constitution of glass.

³ R. W. Strutt, (Lord Rayleigh), *Proc. Roy. Soc.*, 1919, **95**, 476.

⁴ C. V. Raman, *Journ. Optical Soc. America*, 1927, **15**, 185.

⁵ R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1934-5, **1**, 211; 717, 782; 915. 1935, **2**, 221.

2 Specimens Examined.

TABLE I.

Serial No.	Melting No.	Glass contains traces of Al_2O_3 , Fe_2O_3 , As_2O_3 and oxides in :		Density
		more than 10%	less than 10%	
1	25188	SiO_2 , B_2O_3 , Al_2O_3 , K_2O	Na_2O , F	2.3
2	18415	SiO_2 , B_2O_3 , K_2O	Al_2O_3	2.3
3	16776	SiO_2 , K_2O	Al_2O_3 , Na_2O , CaO	2.4
4	23975	SiO_2 , B_2O_3 , ZnO	Al_2O_3 , Na_2O	2.5
5	24906	SiO_2 , B_2O_3	Na_2O , K_2O , BaO	2.5
6	22601	SiO_2 , B_2O_3 , Sb_2O_3	Al_2O_3 , Na_2O , K_2O	2.7
7	23125	SiO_2 , Na_2O , PbO	ZnO	2.7
8	22638	SiO_2 , PbO	Na_2O , K_2O	2.9
9	24464	SiO_2 , ZnO , BaO	B_2O_3 , Na_2O , K_2O , PbO	3.1
10	19510	SiO_2 , PbO	Na_2O , K_2O	3.2
11	23355	SiO_2 , B_2O_3 , BaO	Al_2O_3 , Na_2O	3.3
12	20672	SiO_2 , PbO	B_2O_3 , Na_2O , K_2O	3.4
13	22986	SiO_2 , BaO , PbO	Na_2O , K_2O , ZnO	3.5
14	23441	SiO_2 , PbO	Na_2O , K_2O	3.9
15	23497	SiO_2 , BaO , PbO	Na_2O , K_2O , ZnO	3.9
16	23850	SiO_2 , PbO	Na_2O , K_2O	4.4
17	23590	SiO_2 , PbO	Na_2O , K_2O	5.1

Table I gives the list of seventeen optical glasses and also their composition and density as furnished by the manufacturers. These glasses were manufactured and were presented to Prof C V Raman by Messrs. Schott and Gen. in Jena (Germany). They are in the form of rectangular slabs (3 cm., 3 cm., 2 cm) with all the faces excluding the two end faces well polished. The list comprises a representative collection of optical glasses of widely different densities and composition

3. Preliminary Observations.

The specimen to be examined was kept immersed in dust-free distilled water contained in a rectangular cell. The cell was suitably blackened on the outside excepting for three windows. A narrow beam of sunlight reflected by a single mirror Foucault Heliostat was focussed by means of a

long focus lens. At the focus the light passed through the specimen. The track inside the glass was intensely coloured blue when viewed in the transverse direction. It was of uniform colour and intensity throughout. When the track inside the specimen was viewed in the direction of the incident beam with the aid of a microscope no visible speck was observed, the track being throughout homogeneous.

On examining the light scattered transversely with a double-image prism, the two components observed were very different in colour and intensity, showing thereby that the scattered light was strongly but not completely polarised. The vertical component which was very much more intense was a rich blue in colour. The difference in colour is indicative of a weak fluorescence. Suitable colour filters were introduced in the path of the incident beam to exclude fluorescence. It was found that with an orange filter in the path of the incident beam, the two components of the scattered light were identical in colour for all the specimens.

Table II gives the colours of the vertical and horizontal components of the light scattered transversely by the different optical glasses when a narrow beam of unpolarised white light is passed through them. The refractive index of each specimen for the yellow line of sodium was measured with the aid of a Pulfrich Refractometer.

4 *Measurement of Depolarisation.*

The light from a 25 ampere projection lantern was condensed on a small square aperture (of edge 2 mm). A long focus lens (aperture = 4 cm) served to condense the light emerging out of the aperture on to the glass to be examined which was placed at a distance of about 50 cm. from the lens. A double-image prism was placed in the path of the incident beam by the side of the lens. The scattered light was viewed through another double-image prism. It was found that the fourth image which was the horizontal component of the scattered light arising from the horizontal component of the incident beam was found to be distinctly brighter than either of the middle two equal anisotropic components. This indicated at once that the optical heterogeneity of the glassy medium should no longer be identified as due to the individual molecules, but due to small groups of molecules. Using incident unpolarised light, light polarised with electric vector, vertical and horizontal respectively, the three depolarisation factors ρ_u , ρ_v and ρ_h of the scattered light corresponding to the three cases were measured using a double-image prism and a nicol, with the orange filter in the path of the incident beam. ρ_u and ρ_v are defined as the ratio of the horizontal component to the vertical component, while ρ_h is defined as the ratio of the vertical component to the horizontal component.

TABLE II.

S. No. as in Table I	Density	Refractive Index μ_D	With incident unpolarised white light		
			Colour of the trans- versely scattered light	Colour of the vertical component of the same	Colour of the horizontal component of the same
1	2.3	1.4670	Bluish green	Greenish blue	Yellowish green
2	2.3	1.4925	Bluish white	Blue	Greenish yellow
3	2.4	1.5022	Greenish blue	Blue	Greenish yellow
4	2.5	1.5095	Deep blue	Deep blue	Yellowish brown
5	2.5	1.5269	Green	Bluish green	Yellowish green
6	2.7	1.5294	Blue	Blue	Brown
7	2.7	1.5370	Blue	Blue	Green
8	2.9	1.5449	Blue	Blue	Green
9	3.1	1.5697	Blue	Blue	Yellowish brown
10	3.2	1.5698	Blue	Blue	Greenish yellow
11	3.3	1.5892	Blue	Blue	Yellowish green
12	3.4	1.5983	Blue	Blue	Orange
13	3.5	1.6163	Blue	Blue	Yellowish brown
14	3.9	1.6473	Blue	Blue	Indigo-blue with a pink tinge
15	3.9	1.6498	Blue	Bluish white	Indigo-blue with a pink tinge
16	4.4	1.7130	Blue	Blue	Indigo-blue with a pink tinge
17	5.1	1.7850	Greenish blue	Greenish blue	Greenish yellow

The errors arising from the finite angle of convergence of the incident beam were calculated using Ananthakrishnan's formulæ.⁶ The actual angle of convergence of the beam inside the specimen was equal to $4/50 \times 2/3$ radian. For this particular angle of convergence the corrections for ρ_u and ρ_v were 0.00035 and 0.00017 respectively. Since the observed values of ρ_u and ρ_v were of the order of 0.03 to 0.01 the correction factors could be neglected. In the same way the correction for ρ_h could also be neglected in comparison with the observed value of ρ_h . The values of ρ_u , ρ_v and ρ_h for the glasses examined are given in Table III.

⁶ R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1935, 2, 133.

5. *Intensity Measurements.*

For the measurement of the relative intensity of scattering in these glasses, the photo-electric method was employed. The method consists in allowing the scattered light to fall on a photo-cell which was connected to a direct current valve bridge amplifier. For very weak intensities the deflections of the galvanometer in the amplifier circuit was a direct measure of the intensity of light falling on the photo-cell. Relatively low scattering power in these glasses especially with an orange filter in the path of the incident beam necessitated recourse to sunlight. A parallel beam of sunlight reflected by a single mirror Foucault Heliostat was condensed by means of a long focus photographic lens provided with an iris diaphragm. At the focus the light passed through the specimen of optical glass contained in the cell of water.

TABLE III.

S. No. as in Table I	Refractive index μ_D	With orange filter in the path of the incident beam					
		ρ_v %	ρ_u %	ρ_h (observed) %	ρ_h (calculated) %	$\Delta \rho_u = \rho_u - \frac{2\rho_v}{1+\rho_v}$	Intensity relative to ether = 1
1	1.4670	12.7	26	78	77	3.5	0.8
2	1.4925	12	24	82	81	2.6	1.0
3	1.5022	3.5	8.1	72	72	1.3	1.9
4	1.5095	0.46	1.2	68	62	0.3	3.3
5	1.5269	3.6	8.1	80	75	1.05	0.9
6	1.5294	3.5	7.5	85	82	0.7	1.2
7	1.5370	2.4	5.2	78	82	0.5	2.1
8	1.5449	3.0	6.1	91	91	0.3	2.1
9	1.5697	2.1	4.8	81	75	0.7	1.8
10	1.5698	3.3	7.0	88	84	0.6	1.3
11	1.5892	2.1	4.6	80	82	0.5	1.6
12	1.5983	3.3	7.0	83	84	0.6	1.6
13	1.6163	1.6	3.7	80	74	0.5	2.4
14	1.6473	2.3	5.2	75	76	0.7	..
15	1.6478	2.0	4.5	77	77	0.6	1.9
16	1.7130	2.5	5.3	87	85	0.4	1.8
17	1.7850	2.8	5.9	87	86	0.5	2.2

The whole arrangement was set up inside a dark cabin. The photo-cell was enclosed in a suitable box and was placed in front of the specimen in such a way that when the screen in front of the photo-cell was raised, only the light scattered by the specimen in the exact transverse horizontal direction entered the photo-cell. One of the glasses was kept as the standard for comparison of intensities of scattering. With the orange filter in the path of the incident beam, the glasses were placed inside the cell of water at the focus of the incident beam one after another in quick succession and the corresponding deflections of the galvanometer in the amplifier circuit were recorded. In order to avoid errors arising from the variations in intensity of the incident beam, the readings with the standard glass were taken before and after each one of the glasses was examined. Finally the scattering power of the standard glass was compared with that of pure dust-free ether contained in a double bulb. From the galvanometer deflections the scattering power of each specimen was calculated in terms of that of ether. The values are given in Table III.

6. *Discussion of Results.*

The sixth column in Table III gives the values of ρ_h calculated from the observed values of ρ_u and ρ_v applying the general Reciprocity Relation

$$\rho_u = (1 + 1/\rho_h) / (1 + 1/\rho_v) \quad \dots \quad (1)$$

The agreement between the calculated and the observed values of ρ_h is quite satisfactory.

Almost all the glasses examined are fluorescent. But this fluorescence is rather weak unlike that in ordinary viscous liquids. The colour of the fainter component is found to be largely influenced by this fluorescence and consequently it varies from glass to glass. On spectroscopic examination it is found that this weak fluorescence is mainly due to a Raman effect together with a faint continuous fluorescence band superposed on it. This continuous band which extends over several hundred Angstrom units is found to change its position for different specimens.

The light scattered by these glasses is strongly polarised as is seen from the low value of ρ_u . The rather high value of ρ_u for glasses 1 and 2 may be due to the higher anisotropy of the scattering elements in them. It is to be noted that for all the glasses, the value of ρ_h is definitely less than 100%. This furnishes us for the first time positive evidence for the existence of molecular aggregates in glass, the size of which is not excessively small compared with the wavelength of light. The depolarisation ρ_u arises not only from the anisotropy of the scattering elements but also from their finite size. To a first approximation the anisotropic part of ρ_u can be considered

to be equal to $2\rho_v/(1+\rho_v)$. The difference $\Delta\rho_u$ between the observed value of ρ_u and $2\rho_v/(1+\rho_v)$ represents the depolarisation due to finite size. Values of $\Delta\rho_u$ are given in Table III. $\Delta\rho_v$ is of the order of 0.6%. That this value of $\Delta\rho_u$ is definite but small indicates that the molecular aggregates are not of large size.

Coming to the intensity of scattering, it is seen that the scattering power of glass is of the same order of magnitude as that of an ordinary liquid or liquid mixture, and not as that of an ordinary crystal. A close scrutiny of the figures in Table III reveals the fact that glasses which possess high scattering power give low depolarisation values. Of all the glasses examined the intensity of scattering is maximum for the glass marked 4. The values of ρ_u , ρ_v and ρ_h for this glass are 1.2%, 0.46% and 62%. They are the lowest observed. It can be inferred from this that in addition to the density scattering and orientation scattering, there may exist composition scattering also in glasses as in the case of liquid mixtures. The transverse scattering due to composition fluctuations is in general completely polarised. In spite of the appreciable size of the molecular clusters in glass, the value of ρ_u is diminished by the presence of this composition scattering. Glass can therefore be considered as a mixture of anisotropic molecular aggregates.

The influence of composition of the glass on the depolarisation value and intensity of scattering is very striking. The value of ρ_h is found to diminish with increasing percentage of acidic oxides such as silicon dioxide (SiO_2), boric oxide (B_2O_3), etc., in glass, whereas the value of ρ_h tends to increase as the proportion of basic oxides such as Na_2O , K_2O , PbO etc., increases. In other words, the tendency for the formation of large molecular aggregates is greater for glasses containing more of acidic oxides especially boric oxide and less of basic oxides than for glasses which contain more of basic oxides and less of acidic oxides. Glasses numbered 4, 5, 8, 10, 16 and 17 are illustrative of the above conclusions. The regularity in the dependence of scattering on composition makes it clear that the scattering phenomenon observed in optical glasses is not due to accidental inclusions but is an intrinsic property of glass.

The conclusions of the author regarding the constitution of glass fully substantiate the remarks made by G. Hagg⁷ in his paper on the "Nature of Vitreous State". His remarks can be summarised in a few words as follows:—Glass is an aggregate of large groups. A melt will show tendency for glass formation if it contains large and irregular groups of molecules. The only oxides which are known in the vitreous state are B_2O_3 , SiO_2 , P_2O_5 ,

⁷ G. Hagg, *Journ. of Chem. Phys.*, 1935, 3, 42.

P_2O_5 , GeO_2 , As_2O_3 and As_2O_5 . A melt containing any one of these oxides will easily tend to become glassy on cooling. Glass forming tendency is largest for boric oxide (B_2O_3), which cannot even be obtained in crystalline form. The glass forming ability of the melt will decrease when it is getting more basic.

7 Conclusion.

Important information concerning the constitution of glass and the nature of the vitreous state in general may be expected to result from a detailed study of the Raman spectra as they offer a unique method of investigating these substances which give no X-ray pattern and which will not yield to the usual physico-chemical method of approach. Notwithstanding the inherent difficulties, considerable progress has been made in this direction by Gross and Romanova,⁸ Hollaender and Williams,⁹ Bhagavantam¹⁰ and by Kujuinzelis.¹¹ The Raman lines obtained from glasses are in general broad and diffuse. In addition to these diffuse lines, there is a general background scattering. Consequently the interpretation of the Raman spectra obtained has not been easy. The broadening of the lines as well as the frequency shifts are attributed to the influence of polymerisation. It appears possible that a connection may exist between the width of the Raman bands and the clustering tendency disclosed by the present investigation. Further experimental work in this direction appears desirable.

In conclusion the author takes this opportunity to record his grateful thanks to Prof Sir C. V. Raman, Kt, F.R.S., N.I., under whose guidance the present investigation was carried out.

8 Summary.

A comparative study has been made of the intensity and state of polarisation of the light scattered transversely by a series of seventeen glasses of optical quality with the incident light in different states of polarisation (namely, unpolarised, vertically polarised and horizontally polarised). A weak fluorescence was observed in all the glasses. Measurements of the depolarisation factors ρ_u , ρ_v and ρ_h were made with an orange filter in the path of the incident beam to eliminate fluorescence. ρ_u and ρ_v are found to be of the same order of magnitude as are usually observed in the case of gases. But on the other hand, ρ_h is found to be distinctly less than 100%

⁸ E. Gross and M. Romanova, *Zeits. für Phys.*, 1929, **55**, 744

⁹ A. Hollaender and J. W. Williams, *Phys. Rev.*, 1929, **34**, 380; 1931, **38**, 1739.

¹⁰ S. Bhagavantam, *Ind. Journ. of Phys.*, 1931, **6**, 1.

¹¹ Th. G. Kujuinzelis, *Zeits. für Phys.*, 1935, **97**, 561.

showing thereby the existence of molecular aggregates of size not small compared with the wavelength of light. Since no visible inclusions are observed it is concluded that the scattering in glass is really an internal phenomenon. Measurements of the relative intensity of scattering in these glasses were also made employing the photo-electric method. The influence of composition of the glass on the formation and the size of the molecular aggregates formed is fully discussed. It is found that the tendency for the formation of molecular aggregates increases with an increasing percentage of acidic oxides especially boric oxide, whereas it diminishes when the glass gets more and more basic.

GRAVITY FORMULÆ IN GEODESY; THEIR PRECISION AND INTERPRETATION.

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VARIOUS formulæ for gravity have been introduced from time to time by different geodesists with the result that up till recently, the different countries expressed their gravity anomalies in different terms. Such a state of affairs was obviously highly undesirable for a research into the figure of the Earth, and other correlated problems, where collated data over the whole globe is required. This led to a resolution at the International Union of geodesy and geophysics at Prague (1927), that the advisability of adopting an International gravity formula should be considered, and that such a gravity formula should be brought forward. Although opinions were divided whether in view of the paucity of gravity data, time was ripe for such a gravity formula, still everybody was at one, that uniformity was essential, and that different countries should use the same gravity formula. The International gravity formula was proposed by Heiskanen, and was adopted by the International Union at Stockholm in 1930. This is however not the last word, as Helmert's 1901 and 1915, and Bowie's 1927 formulæ are still in vogue, and there is no doubt that a better formula will be derived when more gravity data are available. Tables have been made for the conversion of gravity from one spheroid to the other. The literature about the derivation of these formulæ is very scattered, and in most cases is not easily accessible, and consequently it is not often realised, that the various formulæ have been derived from quite different considerations.

The object of this paper is to enumerate the important gravity formulæ, and outline the methods of their derivation, discussing the degrees of approximation involved, as well as the interpretation of the various terms.

The following are the main gravity formulæ obtained at different times :—
Helmert 1901. $\gamma_0 = 978.030 [1 + 5302 \times 10^{-8} \sin^2 \phi - 7 \times 10^{-8} \sin^2 2\phi] \dots$ (1)

$$\epsilon = \frac{1}{298.3} = 0.003354, \quad f = -205 \times 10^{-8}.$$

Helmert 1915. $\gamma_0 = 978.052 [1 + 5285 \times 10^{-6} \sin^2 \phi - 7 \times 10^{-6} \sin^2 2\phi]$
 ± 7 ± 4 ± 6 (2)
 $+ 18 \times 10^{-6} \cos^2 \phi \cos 2 (L + 17^\circ)]$
 $\epsilon = 0.00371 + 18 \times 10^{-6} \cos^2 \phi \cos 2 (L + 17^\circ),$
Average $\epsilon = \frac{1}{296.7}, f = -205 \times 10^{-8}$

Berroth. $\gamma_0 = 978.046 [1 + 5296 \times 10^{-6} \sin^2 \phi + 11.6]$
 ± 4.4 ± 7.7 .. (3)
 $\times 10^{-6} \cos^2 \phi \cos 2 (L + 10^\circ) - 7 \times 10^{-6} \sin^2 2\phi]$
 $\epsilon = \frac{1}{297.8 \pm 0.7} + 11.6 \times 10^{-6} \cos 2 (L + 10^\circ),$
 $f = -205 \times 10^{-8}$

Bowie 1917. $\gamma_0 = 978.039 [1 + 5294 \times 10^{-6} \sin^2 \phi - 7 \times 10^{-6} \sin^2 2\phi]$
.. (4)
 $\epsilon = \frac{1}{297.4 \pm 1.0}, f = -205 \times 10^{-8}$

Survey of India, Spheroid II.¹
 $\gamma_0 = 978.021 [1 + 5234 \times 10^{-6} \sin^2 \phi - 6 \times 10^{-6} \sin^2 2\phi]$
.. (5)
 $\epsilon = \frac{1}{292.4}, f = 0$

Best formula for India as available from data till 1929 is
 $\gamma_0 = 978.021 [1 + 5359 \times 10^{-6} \sin^2 \phi - 6 \times 10^{-6} \sin^2 2\phi]$.. (6)
 $\epsilon = \frac{1}{301}, f = 0$

Heiskanen 1924. $\gamma_0 = 978.052 [1 + 5285 \times 10^{-6} \sin^2 \phi + 27 \times 10^{-6} \cos^2 \phi]$
 ± 3 ± 6 ± 3 .. (7)
 $\times \cos 2 (L - 18^\circ) - 7 \times 10^{-6} \sin^2 2\phi]$
 ± 5
Average $\epsilon = \frac{1}{296.7 \pm 0.5}, f = -205 \times 10^{-8}$

Heiskanen 1928. $\gamma_0 = 978.049 [1 + 5293 \times 10^{-6} \sin^2 \phi - 7 \times 10^{-6} \sin^2 2\phi]$
 $+ 19 \times 10^{-6} \cos^2 \phi \cos 2 (L - 0^\circ)]$.. (8)
Average $\epsilon = \frac{1}{297.3}, f = -205 \times 10^{-8}$

International ellipsoid
 $\gamma_0 = 978.049 [1 + 52884 \times 10^{-7} \sin^2 \phi - 59 \times 10^{-7} \sin^2 2\phi]$
.. (9)
 $\epsilon = \frac{1}{297}, f = 0$

ϕ and λ are the geodetic latitude and longitude. Longitudes are reckoned positive E. of Greenwich meridian. ϵ denotes the ellipticity of the spheroid. Meaning of f is made clear later.

There are two main directions, into which the body of research into gravity formulæ may be branched. One is the classical method of Stokes³, Helmert⁴ and Darwin⁴, the other is the modern work of Pizetti, Cassinis and other Continental writers

The historical method of approach consists in writing down the expression for external potential of an attracting system in the form of an infinite series by means of spherical harmonics. If the form of the geoid is

$$r = k (1 + u_2 + u_3 + \dots) \quad \dots \quad \dots \quad (10)$$

and if there are no masses external to it, the potential due to it in external space is given by

$$U = \frac{y_0}{r} + \frac{y_1}{r^2} + \dots$$

Using the condition that the geoid is an equipotential, namely

$$U + \frac{1}{2} \omega^2 r^2 \cos^2 \theta = c,$$

Stokes derived the following expression for U .

$$U = \frac{y_0}{r} + \frac{k y_0 u_1}{r^2} + \dots - \frac{\omega^2 k^5}{2r^3} \left(\frac{1}{3} - \sin^2 \theta \right), \quad \dots \quad (11)$$

where θ denotes the geocentric latitude.

The force of gravity at a point of the geoid is given by differentiating (11) with respect to an element of normal of the geoid. To a first approximation we may take

$$g = - \frac{d}{dr} \left(U + \frac{1}{2} \omega^2 r^2 \cos^2 \theta \right)$$

This fixes the value of gravity on the geoid to be

$$g = G \left[1 - \frac{2}{3} m \left(\frac{1}{3} - \sin^2 \theta \right) + u_2 + 2u_3 + \dots + (n-1)u_n + \dots \right] \quad \dots \quad (12)$$

$$\left. \begin{aligned} \text{where } m &= \frac{\omega^2 k}{G}, \quad y_0 = k \left(c - \frac{\omega^2 k^3}{3} \right), \\ \text{and } G &= \frac{\iint g d\omega}{4\pi} = \frac{y_0}{k^3} - \frac{2}{3} \omega^2 k = \frac{1}{k} (c - \omega^2 k^3). \end{aligned} \right\} \quad \dots \quad (13)$$

The equation of a spheroid correct to first order in ellipticity is

$$r = a (1 - \epsilon \sin^2 \theta) = k (1 - \frac{2}{3} \epsilon P_2),$$

where $\epsilon = \frac{a-b}{a}$, a and b being the semi-axes. k is the radius of a sphere of equal volume.

From (12) we see that gravity on a spheroid is

$$g = G [1 - (\frac{1}{2} m - \epsilon) (\frac{1}{3} - \sin^2 \theta)] \quad \dots \quad (14)$$

If ϕ is the geodetic latitude, then $\theta = \phi - \epsilon \sin 2 \phi$, \dots (15)

and we get $g = G_e (1 + A \sin^2 \phi)$,

where G_e denotes gravity at the equator, and

$$A = (\frac{1}{2} m - \epsilon)$$

Helmert applied (15) to the gravity data at his disposal, and by a least square solution found $A = 0.0052$, and $G_e = 978.06$ gals

We will now discuss the accuracy of this formula.

The correct expression for gravity is

$$g = - \frac{d}{dn} (U + \frac{1}{2} \omega^2 r^2 \cos^2 \theta),$$

the differentiation being along the normal to the spheroid.

If ψ is the small angle between the spheroidal normal and the radius vector

at any point P, the error $= -g_n + g = g_n (\cos \psi - 1) = -g_n \frac{\psi^2}{2}$,

where $\psi = \epsilon \sin 2 \phi + \dots$

Hence the error is of the order $G\epsilon^2 = \frac{1000}{9 \times 10^4} = 0.011$ gals.

This is rather large, considering that nowadays gravity can easily be measured with a probable error of 1 or 2 milligals

The equation of the spheroid being limited to first order terms in ϵ , the error of the radius vector is of order

$$a \epsilon^2 = \frac{20 \times 10^6}{9 \times 10^4} = 200 \text{ feet}$$

In geodesy, this spheroid is used as a reference figure to fix the geoid from which it differs by small amount. An error of 200 feet in the dimensions of the reference figure is not admissible.

Equation (12) has been derived from first order considerations only, terms of second order being neglected

If the figure of the Earth is a triaxial ellipsoid, the mean ellipticity of whose meridians is ϵ , and the ellipticity of whose equator is η , its polar equation may be written as

$$r = k \left\{ 1 + \epsilon \left(\frac{1}{3} - \sin^2 \theta \right) + \frac{\eta}{2} \cos 2 (L - L_0) \cos^2 \theta \right\}, \quad \dots (16)$$

where L_0 is the longitude, in which the semi-major axis lies.

This is derived from (9) by putting

$$u_1 = 0 \text{ and } u_2 = \epsilon \left(\frac{1}{3} - \sin^2 \theta \right) + \frac{1}{2} \eta \cos 2 (L - L_0) \cos^2 \theta$$

Hence gravity on it would be

$$g = G \left\{ 1 + (\epsilon - \frac{5}{2} m) (\frac{1}{3} - \sin^2 \theta) + \frac{\eta}{2} \cos^2 \theta \cos 2 (\mathbf{L} - \mathbf{L}_0) \right\} \dots (17)$$

Gravity formulæ (2), (3), (7) and (8) enumerated above are of this form, and therefore they show that the geoid has the form of a triaxial ellipsoid. It might be mentioned here, that the theory of rotating fluids shows that a triaxial fluid ellipsoid having the velocity, density and dimensions of the earth cannot be in equilibrium. For the earth, both the meridional and equatorial sections are nearly circular, and have a small ellipticity, while the equilibrium ellipsoid cannot have both of its ellipticities small. Hence adoption of a triaxial form of the geoid is contrary to theory.

It was soon realised that the above formulæ were inadequate to satisfy the practical requirements of geodesy, and Helmert and Darwin then proceeded to get the gravity formulæ correct to second order terms in ellipticity. They proceeded along practically identical lines. A short outline of their method is desirable, indeed necessary for a true appreciation of the formulæ.

The potential W_p at a point P external to the geoid due to attracting masses within the geoid is

$$\begin{aligned} W_p &= \iiint \sqrt{R^2 + r^2 - 2 R r \cos \zeta} \, dm \\ &= \sum_{n=0} \frac{y_n}{r^{n+1}} \text{ for } R > r, \quad \dots \dots \dots (18) \end{aligned}$$

$$\text{where } y_n = \int_{r=0}^{\text{geoid}} r^n P_n \, dm \quad \dots \dots \dots (19)$$

R, r are the distances of the point P and an element of attracting mass dm from the centre of mass, and ζ is the angle between the directions of R and r . Choosing origin at the centre of mass of the attracting masses, and axes of inertia as the axes of co-ordinates, the first three terms of (18) can easily be evaluated.

Let (x, y, z) be the cartesian co-ordinates, and (θ, λ) the geocentric latitude and longitude of an element dm of attracting mass.

Now $P_0 = 1$

$$P_1 = \sin \theta \sin \theta_0 + \cos \theta \cos \theta_0 \cos (\lambda - \lambda_0)$$

$$\begin{aligned} P_2 &= \frac{3}{2} (\sin^2 \theta - \frac{1}{3}) (\sin^2 \theta_0 - \frac{1}{3}) + 3 \sin \theta \cos \theta \sin \theta_0 \cos \theta_0 \cos (\lambda - \lambda_0) \\ &\quad + \frac{3}{2} \cos^2 \theta \cos^2 \theta_0 \cos 2 (\lambda - \lambda_0), \end{aligned}$$

and so on.

By our choice of origin and axes of co-ordinates

$$\int x dm = \int r \cos \theta \cos \lambda dm = 0. \quad \text{Similarly } \int y dm = \int z dm = 0$$

$$\int xy dm = \int yz dm = \int zx dm = 0$$

$$A = \int (y^2 + z^2) dm, \quad B = \int (z^2 + x^2) dm, \quad C = \int (x^2 + y^2) dm.$$

$$\text{or } \int x^2 dm = \frac{C - A + B}{2}, \text{ etc}$$

Hence from (19), $y_0 = M$, the total mass of geoid,

$$y_1 = \int r P_1 dm = 0$$

$$y_2 = \int r^2 P_2 dm = \frac{3}{2} \left(\frac{A+B}{2} - C \right) (\sin^2 \theta_0 - \frac{1}{3}) + \frac{3}{2} (B-A) \times \cos^2 \theta_0 \cos 2 \lambda_0.$$

Evaluation of y_3 and subsequent terms becomes very complicated.

$$\text{Hence } W = \frac{M}{r} \left\{ 1 - \frac{3}{2} \frac{K}{r^2} (\sin^2 \theta - \frac{1}{3}) + \frac{3}{2} \frac{B-A}{Mr^2} \cos^2 \theta \cos 2 \lambda \right\} + \frac{y_3}{r^3} + \frac{y_4}{r^4} \\ + \dots + \frac{1}{2} \omega^2 r^2 \cos^2 \theta, \quad \dots \dots \dots (20)$$

$$\text{where } K = \frac{1}{M} \left(\frac{A+B}{2} - C \right).$$

This expression holds for any rotating body.

For a homogeneous spheroid $\frac{x^2+y^2}{a^2} + \frac{z^2}{b^2} = 1$,

$$A = B = \frac{M}{5} (a^2 + b^2), \quad C = \frac{2}{5} M a^2,$$

hence $K = -\frac{a^2 e^2}{5}$, where e is the eccentricity.

The third term obviously vanishes y_3 is also zero.

$$y_4 = \int P_4 r^2 dm = \frac{a^4 e^4}{280} (105 \sin^4 \phi - 90 \sin^2 \phi + 9).$$

We thus deduce the potential of a spheroid to be

$$W = \frac{M}{r} \left\{ 1 + \frac{a^2 e^2}{10 r^2} (1 - 3 \sin^2 \phi) + \frac{a^4 e^4}{280 r^4} (105 \sin^4 \phi - 90 \sin^2 \phi + 9) + \dots \right\}.$$

Helmert assumed in the first instance that the potential of the earth instead of being represented by (19) was

$$U = \frac{M}{r} \left\{ 1 - \frac{3}{2} \frac{K}{r^2} (\sin^2 \theta - \frac{1}{3}) + \frac{3}{2} \frac{B-A}{Mr^2} \cos^2 \theta \cos 2 \lambda + \frac{\omega^2 r^2}{2M} \cos^2 \theta \right\} \dots (21)$$

W and U are nearly equal. The equipotentials, $U = \text{constant}$, are known as 'level spheroids'. It might be pointed out, that these surfaces are not

actual spheroids, but are fairly close approximations to them. Also A, B have now lost their physical significance. They are no more the exact moments of inertia of the masses within the geoid. On these level spheroids, gravity is given by

$$g = \frac{M}{r^2} \left\{ 1 + \frac{3K}{2r^2} (1 - 3 \sin^2 \theta) + \frac{9(B-A)}{4Mr^2} \cos^2 \theta \cos 2\lambda - \frac{\omega^2 r^3}{M} \cos^2 \theta \right\}$$

This formula has never been much in vogue

Helmert next took as an approximation to W,

$$U = \frac{M}{r} \left\{ 1 + \frac{K}{2r^2} (1 - 3 \sin^2 \theta) + \frac{\omega^2 r^3}{2M} \cos^2 \theta + \frac{D}{r^4} (\sin^4 \theta - \frac{2}{3} \sin^2 \theta + \frac{8}{15}) \right\} \dots (22)$$

On reference to (19), we see that only those terms of y_4 have been included, which are independent of λ . The whole of y_4 has not been included, as the equipotentials are intended to be symmetrical with respect to the rotation axis. The y_3 term has also been omitted for the same reason. Neglecting the term containing the angular velocity, formula (22) resembles exactly the expression for the potential of a spheroid at an external point, namely

$$U = \frac{M}{r} \left\{ 1 + \frac{a^2 e^2}{10r^2} (1 - 3 \sin^2 \theta) + \frac{a^4 e^4}{280r^4} (105 \sin^4 \theta - 90 \sin^2 \theta + 9) + \dots \right\}.$$

Let the polar equation of a meridian curve of the equipotential surface

$$u + \frac{1}{2} \omega^2 r^2 \sin^2 \theta = u_0$$

$$\text{be } r = a (1 - P \sin^2 \theta + Q \sin^4 \theta - \dots) \dots \dots (23)$$

Substituting in (22), and using (23), we see that

$$\begin{aligned} a &= \frac{M}{u_0} \left\{ 1 + \frac{K}{2a^2} + \frac{\omega^2 a^3}{2M} + \frac{3D}{35a^4} \right\} \\ P &= \frac{M}{a u_0} \left\{ \frac{K}{a^2} \left(\frac{2}{3} - P \right) + \frac{\omega^2 a^3}{2M} (1 + 3P) + \frac{2}{7} \frac{D}{a^4} \right\} \\ Q &= \frac{M}{a u_0} \left\{ P \left(\frac{2}{3} \frac{\omega^2 a^3}{M} - \frac{3K}{a^2} \right) + \frac{D}{a^4} \right\} \end{aligned}$$

Since, we are now aiming at accuracy upto second order of small quantities, we have to take

$$g^2 = U_1^2 + U_2^2, \text{ where } U_1 = -\frac{\delta}{\delta r} (U + \frac{1}{2} \omega^2 r^2 \cos^2 \theta), U_2 = -\frac{\delta}{r \delta \theta} (U + \frac{1}{2} \omega^2 r^2 \cos^2 \theta).$$

It is found after easy simplification, that the equation of the meridian curve is

$$r = a \{ 1 - (\epsilon - 2\epsilon^2 + \frac{5}{2} \epsilon m + \delta) \sin^2 \theta - (2\epsilon^2 - \frac{5}{2} \epsilon m - \delta) \sin^4 \theta \} \dots (24)$$

and gravity on it is

$$g = G_e \left\{ 1 + \left(\frac{5}{2} m - \epsilon + 6\epsilon^2 - \frac{\epsilon m}{2} - \frac{1}{7} \delta \right) \sin^2 \theta - (7\epsilon^2 - 3\delta) \sin^4 \theta \right\} \dots (25)$$

where G_e is the mean value of gravity on the equator,

$$\left. \begin{aligned} G_e &= \frac{M}{a^3} \left\{ 1 + \epsilon - \frac{3}{2} m - \epsilon^2 - \frac{1}{2} \epsilon m + \frac{3}{4} m^2 + \frac{1}{4} \delta \right\} \\ m &= \frac{\omega^2 a}{G_e} \\ \delta &= \frac{D}{a^4} \\ \frac{3}{2} \frac{K}{a^3} &= \epsilon - \frac{m}{2} - \epsilon^2 + \frac{1}{2} \epsilon m + \frac{3}{4} m^2 + \frac{1}{4} \delta \end{aligned} \right\} \dots \dots \dots (26)$$

To express (25) in terms of geodetic latitude ϕ , we make use of the relation $\theta = \phi - \epsilon \sin 2\phi$, and get

$$g = G_e (1 + A \sin^2 \phi - B \sin^2 2\phi), \quad \dots \dots \dots (27)$$

$$\left. \begin{aligned} \text{where } A &= \frac{3}{2} m - \epsilon - \epsilon \left(\epsilon + \frac{m}{2} \right) + \frac{3}{4} \delta \\ B &= - \frac{7\epsilon^2 - 3\delta}{4} + \epsilon A \end{aligned} \right\} \dots \dots \dots (28)$$

By giving different values to δ in (24) we can get the formula for gravity on an equipotential surface having a known form differing but little from an ellipsoid of revolution.

Darwin's method is practically identical. He starts with a level surface

$$r = a \left\{ 1 - \epsilon \sin^2 \theta + \left(f - \frac{3}{2} \epsilon^2 \right) \sin^2 \theta \cos^2 \theta \right\} \quad \dots \dots (29)$$

and writes its external potential as

$$U = \frac{M}{r} + \frac{\beta P_2}{r^3} + \frac{\gamma P_4}{r^5} \quad \dots \dots \dots (30)$$

The two equations (24) and (29) are identical, if

$$f = \frac{7}{2} \epsilon^2 - \frac{3}{2} m \epsilon - \delta.$$

Proceeding exactly as before Darwin arrived at the equations (27) and (28). In getting g , he also used

$$g^2 = U_1^2 + U_2^2$$

In actual practice, the situation is, that gravity is observed on the earth, and by some suitable method, it is reduced to the geoid. From these values of gravity, the shape of the geoid has to be deduced. We have seen that on the level surface (24),

$$g = G_e [1 + A \sin^2 \phi - B \sin^2 2\phi],$$

where the quantities G_e , A and B are expressible in terms of M , m , ϵ , and δ .

A knowledge of the values of gravity at three places will give us G_e , A and B . However, to obtain reliable values for these constants, they are determined by least squares using as many gravity stations as are available.

B is a small quantity, about $\frac{1}{800}$ times smaller than A, and it was found that its value could not be deduced from the gravity data with any accuracy.

The quantity δ defines the elevation or depression of reference surface (24) from a true spheroid, and is determined from theoretical considerations. Darwin has deduced values of δ (or f) from two quite different assumptions about the internal constitution of the earth. He first assumed Roche's law of density, and obtained $f = -205 \times 10^{-8}$. Then he used Wiechert's law, that the earth consists of a solid core of density 8.206, on which is superposed a mantle of density 3.2, and deduced $f = -175 \times 10^{-8}$. The constant B in the gravity formula expressed in terms of f may be written as

$$B = -\frac{\epsilon^2}{8} + \frac{5}{8} m \epsilon - \frac{3f}{4}.$$

Taking $f = -205 \times 10^{-8}$, $m = \frac{1}{288.41}$, and $\epsilon = \frac{1}{298}$,

we get $B = 7 \times 10^{-6}$.

Hence the quantity $7 \times 10^{-6} \sin^2 2\phi$, which occurs in all gravity formulæ is based on theoretical considerations. The magnitude of this term is of the order $7 \times 10^3 \times 10^{-6} \sin^2 2\phi$. The maximum value that it can attain is 0.007, which is quite appreciable.

Darwin's work shows that the figure 7×10^{-6} for B is quite insensitive to the hypothesis about the internal constitution of the earth. It corresponds to a geoid depressed below an exact spheroid by about 3" in latitude 45°. Considering, however, that it is derived from hypothetical assumption about the variation of density in the earth's crust, it appears a bit pedantic to retain it.

For an exact spheroid, which can be used as reference figure for the earth, $B = 6 \times 10^{-6}$ as we shall show later. This value has been used in the International formula.

Yet another approximation may be taken for W, namely

$$U = \frac{M}{r} \left[1 + \frac{K}{2r^2} (1 - 3 \sin^2 \theta) + \frac{\omega^2 r^3}{2M} \cos^2 \theta + \frac{L}{r^2} \cos^2 \theta \cos 2(L - L_0) \right. \\ \left. + \frac{T}{r^3} \left(\frac{3}{8} \sin \theta - \sin^3 \theta \right) + \frac{D}{r^4} \left(\sin^4 \theta - \frac{3}{4} \sin^2 \theta + \frac{3}{8} \right) \right] \quad \dots \quad (31)$$

Gravity on a level surface whose potential is as above is

$$g = G_e \left\{ 1 + (\beta_2 + \beta_4) \sin^2 \phi + \beta'_2 \cos^2 \phi \cos 2(L - L_0) + \beta_3 \left(\frac{3}{8} \sin \phi - \sin^3 \phi \right) \right. \\ \left. - \frac{\beta_4}{4} \sin^2 2\phi \right\} \quad \dots \quad \dots \quad \dots \quad \dots \quad (32)$$

The equation of the meridian curve is

$$r = a_m \{1 - \alpha \sin^2 \phi + \beta \cos^2 \phi \cos 2(L - L_0) + \gamma (\frac{3}{8} \sin \phi - \sin^3 \phi) + \delta \sin^2 2\phi\} \quad (33)$$

It can be easily verified that these results agree with Stokes' equations, namely that for

$$g = G [1 + u_2 + u_3 + \dots],$$

$$r = R [1 + \frac{5}{2} m (\frac{1}{3} - \sin^2 \phi) + u_2 + \frac{1}{2} u_3 + \dots].$$

The equation to r contains $(\frac{3}{8} \sin \phi - \sin^3 \phi)$. If the northern and southern hemispheres are symmetrical, this term should disappear in r , and therefore also in g

β'_2 is a function of difference $(B - A)$ of the moments of inertia of the level surface

The rigid theory of triaxial ellipsoid gives (as we shall see later),

$$g = g_a \left[1 + \frac{1}{4} (e'^2 + 2\eta') + \left\{ \frac{1}{2} (e^2 + 2\eta) + \frac{e^2}{8} (3e^2 + 4\eta) - \frac{1}{4} (e'^2 + 2\eta') \right\} \sin^2 \phi \right. \\ \left. - \frac{1}{4} (e'^2 + 2\eta') \cos^2 \phi \cos 2L - \frac{e^2}{32} (3e^2 + 4\eta) \sin^2 2\phi \right] \quad \dots (34)$$

In (34), $g_e = g_a \{1 + \frac{1}{4} (e'^2 + 2\eta')\}$

For Helmert's 1915 formula, $g_e = 978.052$,

$$\text{and } -\frac{1}{4} (e'^2 + 2\eta') = +18 \times 10^{-6},$$

$$\text{hence } 978.052 = g_a (1 - 18 \times 10^{-6})$$

$$\text{or } g_a = 978.052 (1 + 18 \times 10^{-6}) = 978.070$$

where g_a is gravity at the extremity of the semi-major axis.

978.052 is mean value of gravity at the equator

$$\text{At the equator, } g = g_a [1 + \frac{1}{4} (e'^2 + 2\eta') - \frac{1}{4} (e'^2 + 2\eta') \cos 2L]$$

$$\text{Mean equatorial gravity} = g_a [1 + \frac{1}{4} (e'^2 + 2\eta')]$$

The second method, and one which is more fundamental is the one propounded by Pizetti⁶ in 1913. It deals with the case of a triaxial ellipsoid, which is a level surface of its own attraction and rotation. Strictly speaking, the assumption that a level surface is an exact ellipsoid is inconsistent with perfect hydrostatic equilibrium, as has been remarked already. Somigliana proceeding on the same lines as Pizetti derived a closed elegant expression for gravity on an ellipsoid, which may be written as

$$g = \frac{(ag_a \cos^2 L + bg_b \sin^2 L) \cos^2 \phi + cg_c \sin^2 \phi}{\sqrt{(a^2 \cos^2 L + b^2 \sin^2 L) \cos^2 \phi + c^2 \sin^2 \phi}} \quad \dots \quad (35)$$

where g_a, g_b, g_c are the values of g at the extremities of the three axes, and (ϕ, L) denote the latitude and longitude respectively

This can be easily verified, because the 3 extremities of the axes are given by $(\phi = 0, L = 0)$, $(\phi = 0, L = 90^\circ)$, and $\phi = 90^\circ$ and when these values are substituted in (35), g assumes the appropriate values.

Somigliana in No. 38 of *Bulletin Geodesique*, 1933 has expanded (35) and has obtained

$$g = g_a \left[1 + \frac{1}{2} (e^2 + 2\eta) \sin^2 \phi + \frac{1}{2} (e'^2 + 2\eta') \cos^2 \phi \sin^2 L + \frac{e^2}{2 \cdot 4} (3e^2 + 4\eta) \sin^4 \phi \right], \quad \dots (36)$$

$$\text{where } e^2 = \frac{a^2 - c^2}{a^2}, \quad e'^2 = \frac{a^2 - b^2}{a^2},$$

$$\eta = \frac{cg_c - ag_a}{ag_a}, \quad \eta' = \frac{bg_b - ag_a}{ag_a}.$$

For a spheroid, η' and c' become zero, and the L -term disappears.

For a spheroid, $g = \frac{ag_e \cos^2 \phi + cg_r \sin^2 \phi}{\sqrt{a^2 \cos^2 \phi + c^2 \sin^2 \phi}}$, where g_e, g_r denote the values of gravity at the extremities of the equatorial and polar axes.

$$\begin{aligned} g &= G_e \frac{1 + (\beta - \epsilon - \epsilon\beta) \sin^2 \phi}{\sqrt{1 - \epsilon} (2 - \epsilon) \sin^2 \phi} \\ &= G_e [1 + \beta \sin^2 \phi - \beta_1 \sin^2 2\phi - \beta_2 \sin^2 \phi \sin^2 2\phi - \beta_3 \sin^4 \phi \sin^2 2\phi - \dots] \end{aligned} \quad \dots (37)$$

$$\left. \begin{aligned} \text{where } \epsilon &= \frac{a - c}{a} \\ \beta &= \frac{g_r - g_e}{g_e} = \frac{1}{2} m (1 - \frac{1}{2} \epsilon - \dots) - \epsilon \\ \beta_2 &= \frac{\epsilon^2}{8} (2\epsilon + 3\beta) - \frac{\epsilon^3}{32} (3\epsilon + 4\beta). \\ &\dots \dots \dots \end{aligned} \right\} \quad \dots \quad \dots (38)$$

If we introduce an auxiliary parameter

$\eta = \frac{cg_r - ag_e}{ag_e}$ instead of β we can write (37) in the form

$$g = g_e \left[1 + \frac{1}{2} (e^2 + 2\eta) \sin^2 \phi + \frac{e^2}{2 \cdot 4} (3e^2 + 4\eta) \sin^4 \phi + \dots \right] \quad \dots (39)$$

W. D. Lambert in *Bulletin Geodesique*, 1931, has introduced another auxiliary function C , and has obtained an expression for g in the form

$$g = G_e (1 + C_2 \sin^2 \phi + C_4 \sin^4 \phi + \dots), \quad \dots \quad \dots (40)$$

where $C_2 = \frac{1}{2} (2mC - e^2) = \frac{1}{2} (e^2 + 2\eta)$

$$C_4 = \frac{e^2}{8} (4mC - e^2), \text{ etc.}$$

and $C = \frac{\eta}{m} + e^2.$

$$\epsilon + \beta = \frac{1}{2} \frac{\omega^2 a}{G_e} \quad \chi(\epsilon) = \frac{1}{2} \frac{\omega^2 a}{G_e} (1 - \epsilon) C(e^2),$$

$$\chi(\epsilon) = 1 - \frac{17}{15} \epsilon - \frac{\epsilon^2}{245} - \dots$$

Formula (37) agrees exactly with Helmert's formula (27), except that it contains terms beyond the third. It can be easily verified that the constants A and B in the two formulæ are identical to the second order of small quantities.

It has been mentioned above that the constants A and G_e are derived from a least square solution, and B is determined from the theoretical value of f . Knowing A, B and δ , we can determine the values of ϵ and m from (24). When m is known, we can get a from the equation $m = \frac{\omega^2 a}{G_e}$, and it appears at first sight that g data provide information not only about the shape of the geoid, but also about its dimensions. The value of a so found is however useless, as m is a small quantity, which gets multiplied by a large number $\frac{G_e}{\omega^2}$, and thus the uncertainty in m is considerably magnified.

Knowing m and ϵ , we see from the equation

$$G_e = \frac{M}{a^2} \left[1 + \epsilon - \frac{3m}{2} + \epsilon^2 - \frac{17}{15} m \epsilon + \frac{9}{2} m^2 \right], \quad \dots \quad (41)$$

that G_e fixes the mass of the earth, and hence its mean density. Amongst the constants in the formula for normal gravity, this is the most important, and has a much greater effect than the others. A glance at the various g formulæ would show that very discrepant values have been obtained for it according to the location and extent of the g data used. The range of values is from 978.021 to 978.052.

Silva in *Accad. Nazionale dei Lincei*, 1930, suggested that $G_e = 978.049$ was the best value, as it makes the mean observed value of gravity equal to the computed mean value. This was adopted at the International Union of geodesy and geophysics at Stockholm in 1930.

Taking $G_e = 978.049$, $\epsilon = \frac{1}{257}$ and $m = \frac{1}{286.36}$, (41) gives the mass of the earth to be 588×10^{19} tons. If we take the mean radius of the earth to be 6,371,221.3 metres we get its mean density to be 5.517 gm/cm³.

The values of G_e found so far show a range of 32 milligals. This corresponds to an uncertainty of $\frac{1}{30,600}$ in the mass and mean density of the earth.

It has been mentioned by Cassinis that once G_e is fixed, it is immaterial, whether we use a reference spheroid, or a triaxial ellipsoid with approximately the same meridional ellipticity, and small equatorial flattening

The reference spheroid chosen is, however, of extreme importance. Values of normal gravity are widely different for different spheroids.

Thus, for Helmert's spheroid (1901), $\epsilon = \frac{1}{298.25}$ and $A = 5302 \times 10^{-6}$

and for Bowie's spheroid, $\epsilon = \frac{1}{297.4}$ and $A = 5294 \times 10^{-6}$.

The difference between the values of the constant A is small as the ellipticities of these spheroids are nearly equal. But for Clarke's 1880 spheroid, $\epsilon = \frac{1}{293.46}$ which gives $A = 5248 \times 10^{-6}$. The value of normal gravity on Clarke's spheroid can therefore differ from that on Helmert's spheroid by 0.050 gals. Table I shows the variation of the constant A with ϵ .

TABLE I

$1/\epsilon$	A	$1/\epsilon$	A
290	$10^{-6} \times 5207$	296	$10^{-6} \times 5277$
291	$10^{-6} \times 5219$	297	$10^{-6} \times 5288$
292	$10^{-6} \times 5231$	298	$10^{-6} \times 5300$
293	$10^{-6} \times 5242$	299	$10^{-6} \times 5311$
294	$10^{-6} \times 5254$	300	$10^{-6} \times 5322$
295	$10^{-6} \times 5266$		

$m = \frac{\omega^2 a}{G_e}$, and strictly speaking, varies for each spheroid. Its approximate

value is $\frac{1}{298}$. A change of 0.5 in $\frac{1}{m}$ produces a change of 0.014 gals. in γ_0 , which is quite considerable. It is satisfactory to take m correct to 0.05. For the International spheroid, $m = \frac{1}{298.25}$, and this value has been used in preparing the table. It is also useful to indicate the variation of A with G_e . A change of 1×10^{-3} in G_e corresponds to a change of 8.85×10^{-6} in A .

The first important thing to notice from gravity formulæ (2), (3), (7) and (8) is, that if we assume a triaxial ellipsoid with semi-axes a, b, c , (where $a > b > c$) as the equilibrium figure of the earth, then $g_c > g_a > g_b$, which is rather unexpected. At first sight, one would expect g_a to be less than g_b .

Next, a comparison of the formulæ (27) and (37) reveals the superiority of the second method over the first. If we start with the closed formula for gravity on a spheroid, we can expand it in series, and take as many terms as are necessary for the accuracy aimed at. To obtain terms beyond the third by the older method requires great labour. G. Cassinis⁷ and W. D. Lambert⁸ have published tables of the values of gravity on the International spheroid. The former has given two sets of tables, giving the numerical values of normal gravity to 3 and 4 places of decimals respectively. For this accuracy the formula

$$\gamma = 978.0490 (1 + 52884 \times 10^{-7} \sin^2 \phi - 59 \times 10^{-7} \sin^2 2\phi)$$

is sufficient

W. D. Lambert has tabulated these values to six places of decimals, and has included the term $c \sin 6\phi$ in the formula

It might be remarked however that with the present degree of accuracy of gravity measurements, the values of normal gravity to 6 decimal places are of academic interest only.

It is important to realise that the International formula is on a different footing to the others. Its dimensions $a = 637,838.8$ metres and $e = \frac{1}{297}$ have been deduced from plumb-line deflections. The constants A and B have been computed by substituting these values in (28). The constant B in the other formulæ has been deduced from theoretical considerations involving assumptions about the internal constitution of the earth, and the constants G_e and A from least square solution

The constants for International spheroid can be computed to any degree of accuracy that we like, but not so for the other formulæ.

$$\text{Thus } \left. \begin{array}{l} A = 0.005,288,38 \\ B = 0.000,005,87 \\ \beta_2 = 0.000,000,022 \end{array} \right\} \text{ for the International spheroid}$$

In the older formulæ, the constants cannot be written to such numerical accuracy, as the probable error of their values deduced from least square solution is in the 5th place of decimals

The values of ellipticity deduced from the different gravity formulæ have been given along with the formulæ. Its values range from $\frac{1}{293}$ to $\frac{1}{280}$, showing that it is very sensitive to the distribution of gravity data. The value $\frac{1}{297}$ adopted for the International formula has been obtained from deflection data in U. S. only, which is only 1.6% of the area of the whole earth. It was adopted not for its own intrinsic merit, but simply (for want of a better value) to ensure uniformity in the expression of gravity anomalies in different countries.

The ideal condition for the determination of the ellipticity is a net of g stations uniformly distributed over the globe. This is a desideratum at present. There are hardly any gravity stations in the Southern hemisphere. Even in the Northern hemisphere, there are immense gaps. But the future outlook is very hopeful, as different countries are at the moment actively engaged in pendulum operations.

In the U. S. S. R., five hundred stations have been occupied within the last ten years, and their present output is about 1200 stations per year. Their objective is to cover Russia with a density of one station per 20 square Kms. With the advent of the static gravity meter, which is a marked improvement on the older pendulum apparatus as regards speed, and the success with the Vening Meenesz's apparatus for getting gravity at sea, time is not far, when the ideal distribution mentioned above will be achieved.

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DERIVATIVES OF SALICYLIC ACID.—PART IX.

Stability of the Sulphonic Acid Group in the 4-Sulphosalicylic Acid.

Part I. Nitration of 4-Sulphosalicylic Acid.

BY N. W. HIRWE AND M. R. JAMBHEKAR

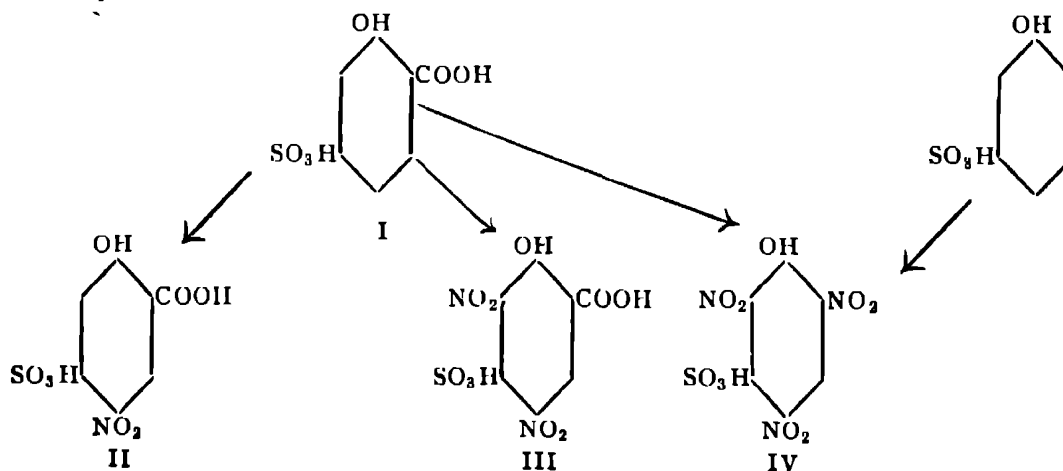
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(Communicated by Dr. T. S. Wheeler, Ph.D., F.I.C., F.Inst.P., M.I.Chem.E.)

It has been found by the previous workers that the sulphonic acid group in either 3-sulpho- or 5-sulpho-salicylic acid can easily be substituted by the nitro group, and if the reaction is carried further, the -COOH group is removed and picric acid is the usual and the only product. Thus Datta and Varma¹ obtained picric acid by the action of nitrous gases on 5-sulphosalicylic acid. Meldrum and Hirwe² obtained 3 : 5-dinitrosalicylic acid by controlled nitration of 5-sulphosalicylic acid.

With the view to study the stability of the sulphonic acid group in 4-sulphosalicylic acid (I), it was treated with nitric acid in acetic anhydride, when nitrosulphosalicylic acid (II) and dinitrosulphosalicylic acid (III) were obtained. On heating (I) with concentrated nitric acid symmetrical trinitro-*m*-phenol-sulphonic acid (IV) was obtained. A similar result was obtained by heating phenol-*m*-sulphonic acid with nitric acid, when a compound identical with (IV) was formed, the barium salt of which has been studied by Berndsen.³



Thus it can be seen that the sulphonic acid group is not always substituted by the nitro group but sometimes appears to be as stable as -COOH .

It enters easily and is as easily substituted when it occupies a position influenced by groups already present, but in positions outside this influence it is difficult to introduce and cannot be easily displaced.

The combined directing influence of the -OH and -COOH groups in salicylic acid is evident in many instances, as also the preference to position -5 over that of -3. When this fact is considered, the constitutions of the nitrosulpho compounds described above require no separate proof.

Respective amino compounds also have been obtained from them.

Experimental

Nitration of 4-sulphosalicylic acid.—4-Sulphosalicylic acid was prepared as described in our previous paper.⁴ It was dehydrated by keeping it over H_2SO_4 for two days.

Acid potassium-4-sulpho-5-nitrosalicylate.—To 4-sulphosalicylic acid (desiccated; 10 g.) dissolved in acetic anhydride (40 c.c.) and well cooled in ice, nitric acid (12 c.c.; sp. gr. 1.4) was slowly added below 5° and the mixture was left for twelve hours in a refrigerator and then at room temperature for twenty-four hours. The separated solid was found to be 4-sulpho-3:5-dinitrosalicylic acid. On diluting the mother liquor with concentrated potassium chloride solution, the acid potassium salt of 4-sulpho-5-nitrosalicylic acid (5.5 g.) was obtained. It crystallised from water in pale yellow plates. On further concentration of the mother liquor, the di-potassium salt (yellow in colour), of the 4-sulpho-3:5-dinitrosalicylic acid, crystallised. The yields of the 4-sulpho-3:5-dinitrosalicylic acid and its di-potassium salt were small. (Found: Equivalent, 317.7; K, 12.0; H_2O , 5.5; $\text{C}_7\text{H}_4\text{O}_8\text{NSK}$, H_2O , requires equivalent, 319.2; K, 12.2; H_2O , 5.6 per cent.)

Neutral barium-4-sulpho-5-nitrosalicylate.—The above potassium salt was neutralised and converted into the barium salt, which is difficultly soluble in boiling water and crystallised from it in orange coloured plates, with a molecule of water, which is not removed even on heating at 200° under reduced pressure. (Found: Ba, 32.9; $\text{C}_7\text{H}_3\text{O}_8\text{NSBa}$, H_2O requires Ba, 33.0 per cent.)

4-Sulpho-5-nitro-salicylic acid was obtained as usual from the above barium salt. It is hygroscopic. It crystallised from water in pale yellow needles, with two molecules of water. It was dried over calcium chloride and then analysed; m.p. $166-167^\circ$. (Found: Equivalent, 148.2; N, 4.6; S, 10.7; H_2O , 11.8; $\text{C}_7\text{H}_5\text{O}_8\text{NS}$, $2\text{H}_2\text{O}$ requires equivalent, 149.6; N, 4.7; S, 10.7; H_2O , 12.0 per cent.)

4-Sulpho-3 : 5-dinitro-salicylic acid—Besides a small quantity obtained above while preparing 4-sulpho-5-nitrosalicylic acid, it was obtained in good yield by employing the same proportions but allowing the temperature to rise freely, which is helped by the considerable evolution of heat, during addition of nitric acid. On cooling it separated as a solid which crystallised from water in pale yellow needles or scales, decomposing above 261°. A further yield is obtained as the di-potassium salt by pouring the mother liquor into potassium chloride solution (Found : S, 10.6 ; N, 9.3 ; $C_7H_4O_{10}N_2S$ requires S, 10.4 ; N, 9.1 per cent.)

Di-potassium-4-sulpho-3 : 5-dinitro-salicylate obtained as above crystallised from water in tiny yellow scales. (Found : K, 20.4 ; S, 8.4 ; $C_7H_2O_{10}N_2SK_2$ requires K, 20.3, S, 8.3 per cent.).

Monopotassium-4-sulpho-3.5-dinitro-salicylate was obtained by acidifying the above salt with hydrochloric acid. It crystallised from water as tiny microscopic needles, yellow in colour (Found : K, 11.3, $C_7H_3O_{10}N_2SK$ requires K, 11.3 per cent.)

Neutral barium-4-sulpho-3 : 5-dinitro-salicylate was obtained by neutralising the acid with barium carbonate. It is more soluble in water than the corresponding salt of the mononitro acid and crystallised from it in red needles, with two molecules of water, which cannot be removed even after heating under reduced pressure. (Found : Ba, 28.3 ; $C_7H_2O_{10}N_2SBa, 2H_2O$ requires Ba, 28.6 per cent.)

2 : 4 : 6-Trinitro-phenol-m-sulphonic acid was obtained by heating the 4-sulphosalicylic acid (desiccated, 10 g.) with concentrated nitric acid (sp. gr. 1.4 ; 15 c.c.) at 100° for an hour. Excess of nitric acid was then evaporated at 100°. The solid obtained crystallised from water in pale yellow cubes, with four molecules of water of crystallisation, m.p. 105°. It is hygroscopic. (Found : N, 11.0 ; S, 8.2 ; H_2O , 18.3 ; $C_6H_3O_{10}N_3S, 4H_2O$ requires N, 11.0 ; S, 8.4 ; H_2O , 18.9 per cent.)

5-Amino-4-sulphosalicylic acid.—To 5-nitro-4-sulphosalicylic acid (5 g.) dissolved in alcohol, ammonium sulphide (5 N ; 30 c.c.) was added and the mixture refluxed for two hours. Having filtered off the sulphur, the mother liquor gave a solid on concentration. It is difficultly soluble in water from which it crystallised as yellowish thin scales, decomposing above 260°. Yield, 4 g. (Found : S, 13.6 ; N, 6.1 ; $C_7H_7O_6NS$ requires S, 13.8 ; N, 6.0 per cent.)

3-Nitro-5-amino-4-sulpho-salicylic acid. To 3 : 5-dinitro-4-sulphosalicylic acid (5 g.) dissolved in alcohol, ammonium sulphide (5 N, 50 c.c.) was added and the mixture heated as above. A solid (3.8 g.) difficultly soluble

in water, from which it crystallised in long yellow needles, was obtained, decomposing above 280°. (Found: S, 11.3; N, 9.9; $C_7H_6O_8N_2S$ requires S, 11.5; N, 10.1 per cent.)

3: 5-Diamino-4-sulphosalicylic acid.—3: 5-dinitro-4-sulphosalicylic acid (2 g) was dissolved in hydrochloric acid and reduced with iron. The solid separating is sparingly soluble in water, from which it crystallised as rectangular dark coloured cubes, decomposing above 290° (Found: S, 12.8; N, 11.4; $C_7H_6O_8N_2S$ requires S, 12.9; N, 11.3 per cent.)

The authors are grateful to Dr. T. S. Wheeler for his great interest in the work.

Summary.

It is shown that the sulphonic acid group outside the directing influences of the -OH and -COOH groups cannot be substituted by the nitro group as in 3-, or 5-sulphosalicylic acids.

Thus on nitration of 4-sulphosalicylic acid, (I) 4-sulpho-5-nitro-salicylic acid, (II) 4-sulpho-3: 5-dinitrosalicylic acid, and (III) 2: 4: 6-trinitrophenol-*m*-sulphonic acid were obtained.

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STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS.—PART I.

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Received February 22, 1936

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1 Introduction

EXTENSIVE investigations by Raman and Krishnan (1928) relating to the electric, optical and magnetic behaviour of liquids have shown that the optical polarisation field surrounding a liquid molecule should, in general, be regarded as anisotropic. A marked diminution in the effective optical anisotropy of certain molecules and a conspicuous failure of the well-known Lorentz formula for the refractivity of certain compounds as we pass from the vapour to the liquid state are usually regarded as typical examples of the experimental facts which receive a satisfactory explanation on this basis. It must, however, be mentioned that the above two tests involve respectively an accurate knowledge of the depolarisation of the scattered light and the refractive index of the substance under question in the vapour state. Recent investigations (Ananthakrishnan, 1935 and H. Volkmann, 1935) have cast some doubt on the reliability of the older results regarding the depolarisation measurements, especially when the values are small, as in the case of gases and vapours, and undisputed values of the refractive indices are available, if at all, only for a few vapours.

A different line of attack would, however, consist in examining the applicability or otherwise of the Lorentz law within the liquid phase itself by altering the temperature. Such a procedure would require an accurate knowledge only of the refractive index and the density of the liquids under investigation at different temperatures, both of which could be obtained with a reasonable certainty. Although reliable data are available for the dependence of density on temperature in many liquids, the variation in refractive index with temperature is known only in a few cases; and even in such cases only over very narrow ranges of temperature. Working on these meagre data alone, Raman and Krishnan (1928) and later Krishnan (1930) have shown that they indicate a break-down of the Lorentz law. In view of the very narrow range in which this aspect of the question has been

examined, it is felt that the majority of evidence available to-day in support of the anisotropic nature of the optical polarisation field depends on the reliability of the measurements of depolarisation of the scattered light and the index of refraction in vapours. Hence, in the present paper extensive data regarding the temperature variation of refractive index for a large number of typical liquids are obtained and, as the variation of density with temperature is already known with sufficient accuracy in these cases, the results are expected to throw light on the validity or otherwise of the Lorentz law without having recourse to the more difficult measurements of the depolarisation of the scattered light and the refractive index of the vapour. The liquids examined here are carbon disulphide, benzene, hexane and carbon tetrachloride. The choice is based on various considerations, such as the varying degrees of optical anisotropy and it is well known that the series constitute a typical set of molecules of special interest from the point of view of light-scattering.

2 Experimental

An Abbe Refractometer is used in measuring the refractive indices of liquids at different temperatures. The refractometer is first standardized by means of the glass test-piece provided with the instrument. The refractometer prisms are then connected with a copper spiral, through which a steady flow of water is maintained with the help of a constant-pressure arrangement. The spiral can be either immersed in cold water or heated by an instantaneous water-heater for low or high temperature work. The instrument is provided with a thermometer reading from 5–70° and refractive index measurements can be made at all intermediate temperatures.

The following tables give the observed refractive indices, densities taken from *I. C. T.* and the molecular refractivities calculated therefrom at different temperatures in the cases of carbon disulphide, benzene, hexane and carbon tetrachloride. The liquids have been purified by distillation at constant boiling point before use.

TABLE I.
Carbon disulphide

Temp.	10	15	20	25	30	35	40	45
Ref. index	1.6360	1.6320	1.6280	1.6240	1.6196	1.6152	1.6108	1.6065
Density	1.2780	1.2705	1.2629	1.2554	1.2479	1.2403	1.2328	1.2252
Mol. Refractivity ..	21.355	21.373	21.393	21.411	21.418	21.426	21.432	21.443

TABLE II.

Benzene

Temp.	15	20	25	30	35	40	45	50	55	60
Ref. index ..	1.5042	1.5012	1.4980	1.4950	1.4920	1.4884	1.4850	1.4820	1.4782	1.4752
Density ..	0.8841	0.8788	0.8734	0.8681	0.8628	0.8575	0.8521	0.8468	0.8414	0.8361
Mol. Refractivity	26.157	26.184	26.204	26.229	26.254	26.256	26.262	26.286	26.288	26.301

TABLE III

Hexane

Temp	15	20	25	30	35	40	45	50	55	60	65
Ref. index ..	1.3700	1.3760	1.3732	1.3705	1.3680	1.3652	1.3625	1.3595	1.3568	1.3540	1.3510
Density	0.6643	0.6596	0.6552	0.6505	0.6459	0.6412	0.6365	0.6318	0.6270	0.6221	0.6172
Mol. Refractivity	29.965	29.960	29.975	29.988	30.019	30.032	30.054	30.052	30.078	30.100	30.108

TABLE IV

Carbon tetrachloride

Temp.	20	25	30	35	40	45
Ref. index ..	1.4610	1.4578	1.4546	1.4513	1.4480	1.4450
Density ..	1.5941	1.5846	1.5749	1.5652	1.5557	1.5461
Mol Refractivity ..	26.480	26.482	26.481	26.477	26.480	26.480

3 *Discussion of Results*

The pronounced temperature variation in the molecular refractivity of CS_2 , C_6H_6 , C_6H_{14} may easily be seen from the tables and from the curves given in Fig. 1. This result definitely shows that the assumption of an isotropic optical polarisation field which forms the basis of the Lorentz law is unjustifiable in some liquids. On the other hand, in the case of carbon tetrachloride the molecular refractivity is more or less constant and it may therefore be concluded that in this liquid, the optical polarisation field is isotropic. Such a conclusion is in agreement with the structure and a number of other experimental facts regarding this molecule. The derivation of the constants of anisotropy of the optical polarisation field and the significance

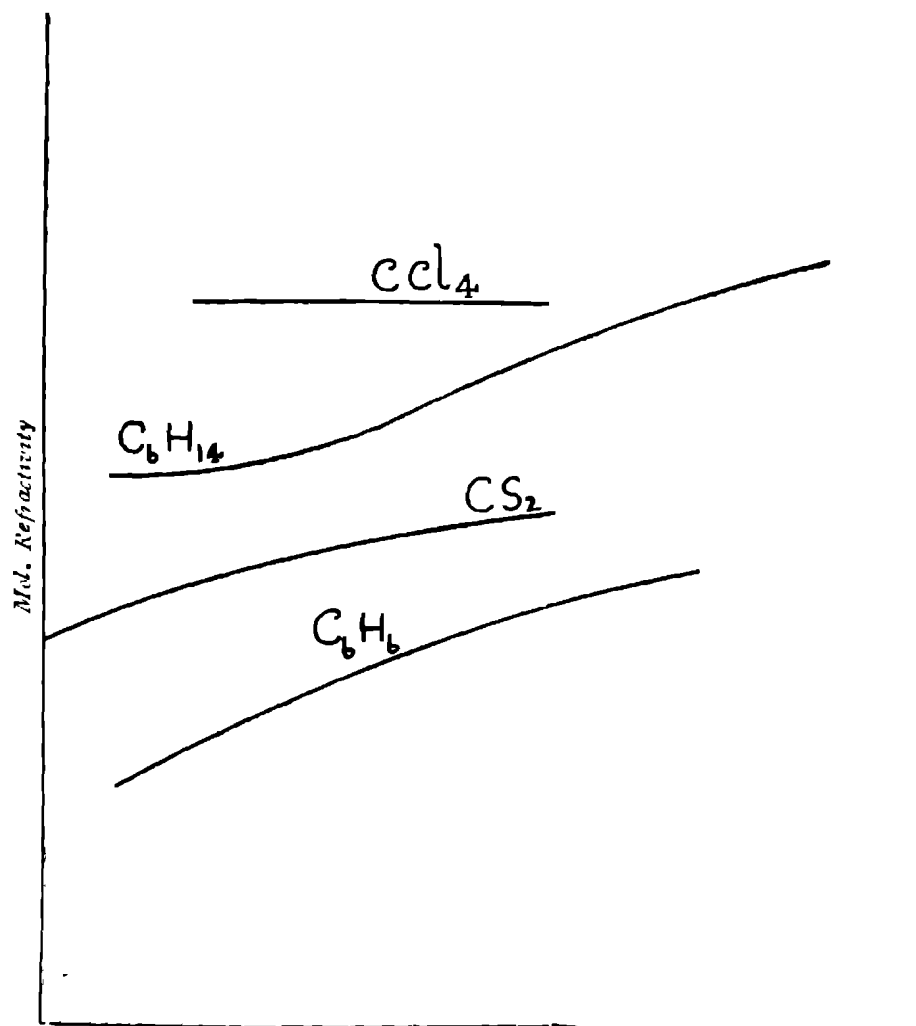


FIG 1 —Temperature

of such constants to the subject of light-scattering will form the subject-matter of Part II.

4 Summary

The molecular refractivity is found to increase with temperature in CS_2 , C_6H_6 and C_6H_{14} liquids. On the other hand, in CCl_4 , it remains constant. These results indicate that the optical polarisation field is anisotropic in the former three liquids whereas it is isotropic in the case of CCl_4 .

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STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS.—PART II.

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1 Introduction.

IN Part I of this series, the molecular refractivity of certain liquids has been determined at different temperatures. The results supported the view that the optical polarisation field surrounding a liquid molecule should, in general, be regarded as anisotropic. In the present paper, it is proposed to calculate the constants, which constitute a measure of such an anisotropy. These constants, along with a knowledge of the compressibilities, etc., may be utilised for determining the depolarisation of the light scattered by the liquid under investigation. Such calculations have been extended to the entire range of temperatures at which data have been gathered in Part I. In this way, we are enabled to study the dependence firstly, of the anisotropic constants and secondly, of the depolarisation of the scattered light, on the temperature of the liquid.

2 Method of Calculation

As will be noticed from Part I, the choice of liquids has been restricted to such cases in which the molecules possess an axis of symmetry. If A , C and C represent the principal optic moments for a vapour molecule and p_1 , p_2 and p_2 the corresponding constants characteristic of the optical polarisation field surrounding the molecule in the liquid state, we have the following relationships:—

$$n_v - 1 = 2\pi\nu_v \frac{A + 2C}{3} \quad \dots \quad \dots \quad \dots \quad (1)$$

$$\frac{10}{6} \frac{r_v}{7r_v} = 2 \left(\frac{A - C}{A + 2C} \right)^2 \quad \dots \quad \dots \quad \dots \quad (2)$$

$$Ap_1 + 2Cp_2 = \frac{3}{\nu_l} - \frac{4\pi(A + 2C)}{n_l^2 - 1} \quad \dots \quad \dots \quad \dots \quad (3)$$

$$p_1 + 2p_2 = 4\pi \quad \dots \quad \dots \quad \dots \quad (4)$$

n_v , ν_v and r_v represent respectively the refractive index, number of molecules per c.c. and the depolarisation of the transversely scattered light in the vapour state. A knowledge of these quantities will enable us to calculate A and C for the various molecules from equations (1) and (2). Substituting these in equations (3) and (4), we obtain the values of p_1 and p_2 after replacing ν_l

and n_l , the number of molecules per c.c. and the refractive index respectively in the liquid state by the observed values. The constants of the anisotropic polarisation field so derived may be made use of in calculating the depolarisation of the transversely scattered light in the liquid state with the help of the following formula :

$$r_l = \frac{2\nu_l F}{kT\beta \left(\frac{n_l^2 - 1}{4\pi}\right)^2 + \frac{7}{3} \nu_l F}$$

where

$$F = \frac{1}{18} (A' - C')^2; A' = A \left(1 + p_1 \frac{n_l^2 - 1}{4\pi}\right), \text{ etc.}$$

It may be noted that by making $p_1 = p_2 = \frac{4\pi}{3}$, all the above formulæ reduce to the usual expressions characteristic of the isotropic optical polarisation field. The derivation of the above equations is contained in a large number of papers dealing with the subject of light-scattering (Raman and Krishnan, 1928) and hence will not be repeated here. By repeating this process for each one of the temperatures, we obtain values for the constants p_1 and p_2 and for r_l the depolarisation of the light scattered by the liquid at different temperatures. The latter have also been determined experimentally at some convenient temperatures in the present investigation. In the following tables θ represents the temperature on the centigrade scale and β the compressibility. p_1 and p_2 , the constants of the polarisation field, have been given to three places of decimals only for purposes of calculation and to bring out the trend of variation in them more prominently. Their absolute values are not significant to such an extent.

3 Results.

TABLE I.

Carbon disulphide.

$$C = 5.892 \times 10^{-24}, A = 14.426 \times 10^{-24}, (n_v - 1) \times 10^6 = 1485, \nu_v = 0.111$$

θ	10	15	20	25	30	35	40	45
n_l	1.6360	1.6320	1.6280	1.6240	1.6196	1.6152	1.6108	1.6065
p_1	2.866	2.866	2.900	2.926	2.926	2.936	2.936	2.936
p_2	4.852	4.852	4.835	4.822	4.822	4.817	4.817	4.817
p_2/p_1	1.692	1.692	1.667	1.647	1.647	1.640	1.640	1.640
$\beta \times 10^{12}$	92.7	..	100.0
100 r_l calc.	61.8	..	60.3
100 r_l obs.	65.3	..	63.5

TABLE II.

Benzene

$$C = 12.828 \times 10^{-24}, A = 6.475 \times 10^{-24}, (n_D - 1) \times 10^6 = 1820, r_D = 0.0445.$$

θ	15	20	25	30	35	40	45	50	55	60
n_D ..	1.5042	1.5012	1.4980	1.4950	1.4920	1.4884	1.4850	1.4820	1.4782	1.4752
p_1 ..	6.940	6.866	6.784	6.764	6.742	6.736	6.705	6.662	6.658	6.642
p_2 ..	2.815	2.852	2.893	2.903	2.914	2.917	2.933	2.954	2.956	2.964
p_1/p_2	2.465	2.407	2.344	2.330	2.313	2.309	2.286	2.255	2.252	2.240
$\beta \times 10^{12}$	90.75	94.50	98.25	102.00	106.00	110.00	114.50	119.00	123.50	128.00
$100r_l$ calc.	40.2	39.9	39.7	39.0	38.2	37.4	37.3	36.3	35.5	34.8
$100r_l$ obs.	42.8	40.6	36.7

TABLE III.

Hexane.

$$C = 10.694 \times 10^{-24}, A = 14.473 \times 10^{-24}, (n_D - 1) \times 10^6 = 2032, r_D = 0.115$$

θ	15	20	25	30	35	40	45	50	55	60	65
n_D ..	1.3790	1.3760	1.3732	1.3705	1.3680	1.3652	1.3625	1.3595	1.3568	1.3540	1.3510
p_1 ..	1.998	1.985	1.971	2.063	2.252	2.315	2.432	2.408	2.548	2.673	2.707
p_2 ..	5.286	5.203	5.299	5.244	5.159	5.128	5.069	5.081	5.011	4.949	4.932
p_2/p_1 ..	2.646	2.666	2.688	2.518	2.290	2.215	2.084	2.110	1.966	1.851	1.821
$\beta \times 10^{12}$	157	206
$100r_l$ calc. .	..	7.5	7.8
$100r_l$ obs.	9.4	8.2

4 Discussion of Results.

(a) *Carbon disulphide, benzene and hexane.*—As has already been pointed out, the polarisation field in these three substances is to be regarded as anisotropic contrary to the case of CCl_4 . These substances are therefore dealt with here and CCl_4 will be considered separately in a subsequent paragraph. Tables I, II and III show that the ratio p_1/p_2 in the case of benzene and p_2/p_1 in the cases of CS_2 and C_6H_{14} tends to diminish with increasing temperature. This indicates that with increasing temperature the polarisation field is becoming more and more isotropic as may be expected. Similar results have

been obtained by Krishnan and Ramachandra Rao (1929) from a consideration of the variation of depolarisation of scattered light with temperature. Hexane has been studied by these authors and the results obtained in this investigation are in fair agreement with those reported earlier by them. It may be mentioned here that benzene, carbon disulphide and hexane are typical examples in which the light scattering experiments (Ramachandra Rao, 1927) show that the optical anisotropy increases with increasing temperature. This result is consistent with the observed approach of the ratio p_1/p_2 to unity and a consequent increase in the molecular refractivity with increasing temperature. On the contrary, liquids are known, in which the effective optical anisotropy decreases with increasing temperature and in such cases deviations from the Lorentz law of an opposite type should be expected. Examples of this kind are some of the fatty acids which are characterised by a marked degree of association. These liquids are under investigation and the results will form the subject-matter of a further communication.

(b) *Carbon tetrachloride*—It will be noticed from the results given in Part I that the molecular refractivity of this substance is more or less constant with temperature. This means that the polarisation field surrounding the CCl_4 molecules is isotropic. Such a conclusion is in perfect agreement with the tetrahedral structure of the molecule. This view has an important consequence regarding the depolarisation of the scattered light in the vapour state and its relation to that observed in the liquid state. In the case of an isotropic polarisation field the formula connecting the two may be given as

$$\frac{RT\beta}{N} \nu_l \frac{r_l}{6 - 7r_l} = \frac{r_v}{6 - 7r_v}.$$

Taking the depolarisation of the liquid as 0.04 and the compressibility as 105×10^{-12} , the value of r_v may be calculated to be 0.0011. This result is in marked disagreement with the hitherto accepted values for the depolarisation of the light scattered by CCl_4 vapour, thus definitely not supporting the idea of a perfectly isotropic polarisation field in CCl_4 . On the other hand, more recent measurements of Ananthakrishnan (1935) show that the upper limit for the depolarisation in this case is only 0.0015. This figure is in excellent agreement with the calculated value and supports strongly the view that the optical polarisation field is isotropic. If the polarisation field is isotropic, one would expect the molecule also to be optically isotropic and hence the origin of this small depolarisation remains a mystery. It may perhaps be attributed to the isotopic molecules or to the admixture of depolarised Raman radiations as has been done by other investigators on previous occasions.

5. Summary.

From a knowledge of the molecular refractivities at different temperatures, the anisotropic constants of the optical polarisation field are calculated in CS_2 , C_6H_6 and C_6H_{14} . It is found that the polarisation field becomes more and more isotropic with increasing temperature.

From these constants, the dependence on temperature of the depolarisation of scattered light in these liquids is also deduced. Experimental observations, made at some convenient temperatures, are compared with the calculations.

Evidence in support of the view that the optical polarisation field in CCl_4 is isotropic is presented.

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THE ALKALOIDS OF HOLARRHENA ANTI-DYSENTERICA.

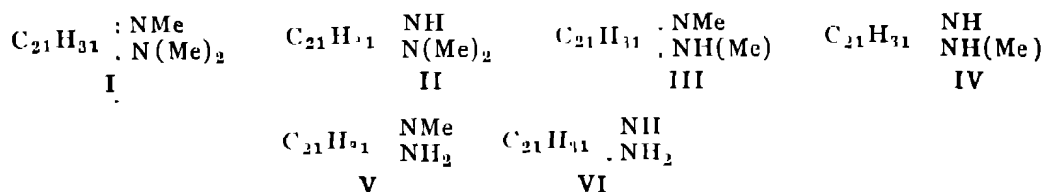
Part IV. The Occurrence of Two Further New Bases in the Bark of Indian Holarrhena and their Relationship to Conessine and Holarrhimine.

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THERE are six different bases theoretically possible according to the number and position of the methyl groups attached to the two nitrogen atoms in the conessine nucleus, $C_{21}H_{31}N_2$. Of these the di-tertiary base, conessine, occurs in the Indian Holarrhena bark to the extent of about 0.4 per cent. The bases, conessimine,¹ iso-conessimine and conimine,² isolated later from the bark and the seeds of the plant in about one-tenth of the yield of conessine, proved to be the nor-bases of conessine answering respectively to the formulæ II, III, and IV, as appeared probable through their methylation to conessine³ and was later definitely established by the N-demethylation of conessine to iso-conessimine and conimine, with the help of BrCN.⁴



It appeared interesting to investigate at this stage, if the two remaining bases, V and VI, were also present in the plant, and if they could, by a suitable method of further demethylation, be directly obtained from it. The isolation or synthesis of the completely demethylated base VI was of particular interest owing to its apparently simple relationship to the oxygenous base holarrhimine, $C_{21}H_{36}ON_2$,⁵ whose molecular formula differed from it by one H_2O .

Attempts to synthesise the two bases have not yet fructified. It has, however, been possible to isolate from the mother liquors of holarrhimine

¹ *J. Ind. Chem Soc.*, 1932, 9, 553

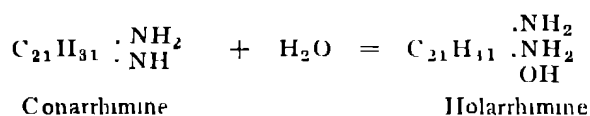
² *Ibid.*, 1934, 11, 283.

³ Ref. 2.

⁴ *Ibid.*, 1934, 11, 787.

⁵ Ref. 1.

sulphate two bases whose hydrochlorides were fairly soluble in water but insoluble in 10 per cent. HCl, and which appear, partly on indirect evidence, to conform to the formulæ V and VI. These two bases which the author proposes to name as conamine and conarrhimine, taking into consideration their apparent relationship to conimine and holarrhimine respectively, were separated from each other by fractional crystallisation from petroleum ether in which conamine is more easily soluble than conarrhimine. The former, however, was too little in quantity to admit of a detailed study and the latter, conarrhimine, could not be obtained free from holarrhimine, into which it is slowly converted in the process of purification through absorption of moisture during repeated crystallisation from hot solvents



In the course of this work, the author was forced to the conclusion that conarrhimine and holarrhimine form eutectic mixtures melting sharply, like any other bases of this series, at 160° and 175°. The study of these two mixtures which are both completely converted into holarrhimine on heating in moist ethyl acetate solution on the water-bath, explains the isolation of kurchicine by Ghosh⁶ and later by Bertho and co-workers^{7*}. But although attempts to isolate pure conarrhimine have failed, its reaction product with nitrous acid, which was got in sufficiently pure condition for analysis, establishes its presence in the plant. In fact it is holarrhimine whose natural occurrence becomes doubtful in the face of the above observations, but the ease with which conarrhimine is converted into holarrhimine makes it very probable that both these bases are originally present in the *Holarrhena* bark.

The five active hydrogen atoms in the above formula for holarrhimine were established by the formation of tetra-N-methyl holarrhimine and subsequent acetylation and benzylation of its hydroxyl group. The diprimary character of holarrhimine was also indicated by its reaction with nitrous acid, whereby a nitrogen-free substance (described in a separate communication was obtained, contrary to the suggestion contained in Part I⁸ (Siddiqui and Pillay, *loc. cit.*) that the non-basic oily product obtained in this reaction

⁶ *Ibid.*, 1928, 5, 477

⁷ *Ber.*, 1933, 66, 786

* The latter authors' konkurchicine (C₂₀H₄₂N₂) m.p. 153° may also prove on further investigation in the light of these findings to be perhaps a more uniform sample of conarrhimine, while their conessidine (C₂₁H₄₂N₂) m.p. 123°, may eventually prove to correspond to one of the two mono methyl bases conamine and conimine (C₂₂H₄₀N₂), melting at 130° and 134° respectively

⁸ Ref. 1.

could be a mixture of mono- and di-nitroso derivatives which failed to crystallise on that account and was not tested any farther. The same authors had also noted only 3 as against 5 active hydrogens in holarrhimine. In view, however, of the experimental evidence above and a fresh corroboration of the earlier finding in respect of the active H determination after Zerewitinoff, the negative error in the active H values has to be explained as being very probably due to the fact that on mixing the magnesium methyl compound in amyl ether solution with the pyridine solution of holarrhimine the latter is partly thrown out of the reaction medium owing to its sparing solubility in amylether.

It may thus be concluded from the foregoing observations, that conarrhimine forms the mother base of the alkaloidal constituents of *holarrhena antidysenterica*, through direct step-wise methylation on the one hand, and on the other through the hydrolysis of its nitrogen ring to holarrhimine, which may very possibly be the starting point of another series of methylation products, whose occurrence in the bark becomes quite plausible in view of the finding that the yield of tetra-N-methyl holarrhimine from the direct methylation of the total alkaloids is far in excess of the yield of holarrhimine in the same sample of the bark (*vide* experimental). Holarrhimine also may be the source of several oxidation and degradation products, which the author has reason to suspect in the bark but which have not so far been obtained sufficiently pure for communication. One such degradation product may be "lettocine" $C_{17}H_{25}O_2N$, lately reported by Peacock and Chaudhri⁹ but in so far as the holarrhena bases invariably crystallise in well-defined forms and are colourless in state of final purity, lettocine also, which is reported as a "light brown, microcrystalline powder," cannot be considered sufficiently pure to give a dependable molecular formula. Discussing these possibilities, it may also be stated here, that the isomerisation of conessine and its nor-bases¹⁰ made the author suspect the presence of the iso-bases in the *Holarrhena* bark, but a long and careful search for them in the total alkaloids from 30 Kg of bark has forced a contrary conclusion.

Experimental.

Isolation of the bases—From the mother liquors of the insoluble holarrhimine sulphate described in Part I (*loc cit*) a fraction of petroleum ether insoluble hydrates was obtained which yielded about 10 gms. of a hydrochloride, soluble in water and insoluble in 10 per cent. HCl. After repeated fractional crystallisation from petroleum ether, with addition of very little

⁹ J. C. S., 1935, 734.

¹⁰ *Proc. Ind. Acad. Sci.*, 1935, 2, 426.

quantities of ethyl acetate, conamine, finally melting at 130° and giving a depression of 15° with conimine was obtained from the more soluble end fraction. (Yield: 1 g., 0.3 per cent. of total alkaloids) The less soluble fraction yielded, after repeated alternate crystallisations from acetone and ethyl acetate, a white crystalline base melting at $158-60^{\circ}$. (Yield: 3 g., 1 per cent. of the total alkaloids.)

The residue from the mother liquors of holarrhimine (Part I, *loc cit.*) melted slowly at $140-65^{\circ}$. This yielded through repeated fractional crystallisation from ethyl acetate and acetone after its initial exhaustion with petroleum ether, a base melting at $173-75^{\circ}$, and apparently corresponding to kurchicine

Conamine— $C_{22}H_{36}N_2$, crystallises from petroleum ether, acetone, and ethyl acetate in clusters of slender needles, m.p. 130° . It is fairly soluble in all the organic solvents, less so in petroleum ether. In 1 per cent. absolute alcoholic solution it showed $[\alpha]_D^{25} = -19^{\circ}$ as against -30° noted for conimine. (Found: C, 79.90, 79.85; H, 11.4, 11.3; N, 7.8; $N-CH_3$, 4.4; $C_{22}H_{36}N_2$ requires C, 80.5; H, 11.0, N, 8.5; CH_3 for 1 $N-CH_3$, 4.6 per cent.) It forms a water soluble and 10 per cent HCl insoluble white, crystalline hydrochloride and also other salts, but a full characterisation of the base and the salts had to be postponed for the present owing to lack of sufficient quantity. A further differentiation between conamine and conimine was, however, established through the fact that on heating in moist ethyl acetate to dryness on the water-bath, conimine remained unchanged while conamine was converted into a high melting product (m.p. $220-40^{\circ}$) which could not be sufficiently purified or studied owing to lack of enough quantity but which may bear a similar relationship to conamine as holarrhimine does to conarrhimine.

The eutectic mixtures of conarrhimine and holarrhimine.—The base melting at $159-60^{\circ}$ crystallises in clusters of white, well-defined needles from acetone and ethyl acetate in which it is distinctly more soluble than holarrhimine. In 1 per cent. absolute alcoholic solution it showed $[\alpha]_D^{31} = -20^{\circ}$ as against $[\alpha]_D^{35} = -11^{\circ}$ for holarrhimine and $[\alpha]_D^{35} = -10^{\circ}$ noted for $173-75^{\circ}$ base in parallel observations. In 1 per cent. chloroform solution the $159-60^{\circ}$ base showed $[\alpha]_D^{34} = -29^{\circ}$ as against $[\alpha]_D^{25} = -14^{\circ}$ for holarrhimine reported in Part I (*loc cit.*). After drying to constant weight over phosphorous pentoxide at 100° *in vacuo* (Found: C, 77.26, 77.32; H, 10.94, 11.15; N, 7.46; $C_{21}H_{34}N_2$ requires C, 80.3, H, 10.8; N, 8.9 ($C_{21}H_{36}ON_2$ requires C, 76.7; H, 11.0; N, 8.1; a mixture of 2 parts $C_{21}H_{36}ON_2$ and 1 part $C_{21}H_{34}N_2$ requires C, 77.9; H, 10.9; and N, 8.3 per cent.). The base melting at 160° thus appears to be a mixture of about 2 parts of holarrhimine and 1 part of conarrhimine.

On repeatedly heating the 160° base (1 g.) in ethyl acetate solution over a layer of water to dryness on the water-bath, the residue which was very slightly coloured, melted at 180°-82°, gave no depression with holarrhimine, melting at 182-83°, and showed within limits of error the same rotation as holarrhimine. After drying to constant weight at 100° *in vacuo* (Found: C, 75.3; H, 10.9; N, 8.0; holarrhimine, $C_{21}H_{31}ON_2$ requires C, 75.9; H, 10.8; N, 8.4. Before heating with water the 160° base gave C, 77.32; H, 11.15; N, 7.46 per cent.). The base melting at 173-75° also gave holarrhimine on heating with ethyl acetate and water as described above, the identity in this case being fixed through the mixed melting point and optical activity.

The salts of the 160° base crystallise in well-defined forms, the Pt value of the platinate corresponding to the value theoretically required.

Reaction product of conarrhimine and nitrous acid—*Nitroso-oxyapo-conarrhimine*.—To test the presence of conarrhimine in the combined mother liquors of conamine at 160° base the residue from these mother liquors was treated in acetic acid solution with excess of sodium nitrite, and the reaction mixture shaken out with ethyl acetate, whereby the basic reaction product of conamine $C_{21}H_{31} \begin{smallmatrix} - NH_2 \\ > NCH_3 \end{smallmatrix}$ and nitrous acid: $C_{21}H_{31}OH : NCH_3$ remained in the aqueous acidic layer. The ethyl acetate containing the non-nitrogenous product, $C_{21}H_{31}(OH)_3$ (discussed in a later communication) from holarrhimine $C_{21}H_{31}OH \begin{smallmatrix} NH_2 \\ .NH_2 \end{smallmatrix}$ and the mono nitroso non-basic derivative $C_{21}H_{31} \begin{smallmatrix} :N.NO \\ .OH \end{smallmatrix}$

from conarrhimine $C_{21}H_{31} \begin{smallmatrix} - NH_2 \\ > NH \end{smallmatrix}$, for which the name nitroso-oxy-apo-conarrhimine is suggested, was washed with water and alkali, dried and freed of the solvent. The residue was taken up in dry petroleum ether, which kept holarrhol in solution and yielded the nitroso product as a slightly coloured, crystalline powder, which stuck to the sides at 145° and melted giving a meniscus at 160-63° (Found: C, 73.46; H, 9.63; N, 7.43; $C_{21}H_{31} \begin{smallmatrix} :N.NO \\ OH \end{smallmatrix}$ requires C, 73.25, H, 9.30; N, 8.13 per cent.). Nitroso-oxy-apo-conarrhimine is sparingly soluble in petroleum ether, fairly soluble in all the other organic solvents and insoluble in water or dilute acids or alkalies.

Methylation of Holarrhimine: Tetra-N methyl holarrhimine.—1 g. holarrhimine was refluxed at 100° with 6 mols. each of formaldehyde (40%) and formic acid for about an hour, till no more carbon dioxide evolved. The pale yellow treacly reaction product was dissolved in water and treated with sodium sulphate solution to remove the very sparingly soluble sulphate of

any unchanged holarrhimine, but no precipitate was formed. The base was then liberated with caustic soda solution and taken up in acetic ether. On drying over sodium sulphate, removing the solvent and cooling the hot alcoholic solution of the residue, tetra N-methyl holarrhimine crystallised in colourless prismatic rods, melting at 233-35° (yield 0.9 g. 85 per cent. of theory).

Also on direct methylation of total alkaloids from 2 kg Holarrhena bark with excess of formaldehyde and formic acid and working up the petroleum ether insoluble portion of the resultant product, tetra N-methyl holarrhimine was obtained in a fairly large yield (about 0.15 per cent on the weight of the bark while the yield of holarrhimine in the same sample was noted as 0.05 per cent.).

Characterisation of Tetra N-methyl Holarrhimine and its Derivatives.—

Tetra N-methyl holarrhimine, $C_{25}H_{44}ON_2$ (Plate XVII) m p. 233-35° is readily soluble in chloroform, fairly soluble in hot ethyl alcohol and methyl alcohol, less so in the cold, difficultly soluble in benzene, acetone and ethyl acetate, nearly insoluble in ether and petroleum ether. It showed in 1 per cent. absolute alcoholic solution $[\alpha]_D^{31} = -45.5^\circ$. In sulphuric acid conc it dissolves to a colourless solution on warming and slowly develops a reddish orange colour which fades on addition of water. (Found C, 77.4, 77.2, H, 11.2, 11.2; N, 7.2; N-CH₃ after Herzig and Meyer 15.7; $C_{25}H_{44}ON_2$ requires C, 77.3, H, 11.3; N, 7.2; CH₃ for 4 N-methyls 15.5 per cent.)

—*hydrochloride* came out on adding together the components in ethereal solution in aggregates of colourless short needles, easily soluble in alcohol and water, insoluble in acetone and ether, and melting with frothing at 315-16°.

—*hydroiodide*.—On adding KI solution to an acetic acid solution of the base the hydroiodide directly crystallised out in bundles of feather-like aggregates of short, tapering prismatic rods sparingly soluble in water and alcohol in the cold, fairly soluble in the hot and melting with frothing at 302-3°.

—*hydrobromide*, prepared similarly as the hydroiodide, came out in short scattered needles, sparingly soluble in alcohol, a little more soluble in water than the hydroiodide and melting at 306-7°.

—*picrate*, was obtained by adding aqueous picric acid to the aqueous solution of the hydrochloride and crystallising the precipitate from hot water, when it formed a bright yellow crystalline powder. It is fairly soluble in hot alcohol, very sparingly in hot water, sticks to the sides at 225° and melts at 272-75°.

—*chloroplatinate* came out on adding 10 per cent platonic chloride to an aqueous solution of the hydrochloride, as an amber coloured granular

precipitate which crystallised on keeping, in aggregates of prismatic rods m.p. 251-52° (Found: 24.46; $C_{25}H_{44}ON_2 \cdot 2HCl \cdot PtCl_4$ requires Pt 24.44 per cent.)

—*methiodide*.—0.15 g. base was treated with 4 mol. methyl iodide in 3 c.c. chloroform solution. The reaction did not proceed at room temperature as quickly as in case of the other bases of the series, but a deposit of colourless crystals settled down overnight, which developed farther on adding a little benzol to the solution. After keeping it again overnight the crystalline deposit was filtered and washed repeatedly with chloroform, m.p. 283-85°. The residue from the filtrate gave through benzol the main quantity of the methiodide as a white crystalline powder which after being well washed with benzene melted with frothing at 286-87° (total yield, 0.18 g.). On analysis this was found to be the mono methiodide of the tetra N-methyl holarrhimine, which apparently does not easily add a sixth methyl owing to the existing load of the N-methyl groups in the molecule (Found: N—CH₃, 14.15; I, 24.37; $C_{26}H_{47}ON_2I$ requires for 5 methyls CH₃, 14.15; I, 23.95 per cent.). The mono methiodide is easily soluble in alcohol, sparingly in water, and on evaporating down the aqueous solution forms a network of slender needles. On slow evaporation it crystallises out in aggregates of stout prismatic rods and conical prisms

Benzoyl tetra N-methyl holarrhimine—0.15 g. base was shaken up with 20 per cent. caustic soda solution and 5 c.c. (10 mols.) of benzoyl chloride at room temperature. To the reaction mixture was added a large quantity of water and the insoluble, white cheesy mass was taken up in ether and shaken out with dil. HCl and water. On making the acidic solution alkaline with caustic soda, without first removing the dissolved ether, the benzoyl base came out as a white crystalline mass, which when washed with water and dried, melted at 170-72°. On recrystallisation from a mixture of ether and petroleum ether it came out in brooms and stars of broad tapering needles, soluble in alcohol and ether, less so in petroleum ether and melting sharply at 176° (Yield, 0.15g.) (Found: C, 77.54; H, 9.8; N, 5.93; $C_{25}H_{43}N_2OC_6H_5$ requires C, 78.04; H, 9.75; N, 5.69 per cent.).

—*hydrochloride* came out on bringing together the components in ethereal solution as an oil. On washing with acetone and drying *in vacuo* it formed a hygroscopic white crystalline powder, shrinking at 163° and melting with frothing at 237-38°. It is exceedingly soluble in alcohol and water, but on adding dil. HCl to the aqueous solution it is thrown out as a snow-white mass formed of aggregates of slender tapering needles. (Found: Cl, 12.33; $C_{25}H_{42}N_2CO \cdot C_6H_5HCl$ requires Cl, 12.56 per cent.).

—*picrate* prepared by adding aqueous picric acid to the aqueous solution of the hydrochloride formed a lemon-yellow crystalline powder, fairly soluble

in acetone and alcohol, very sparingly in water. It gave off moisture from 105-160° and frothed up with darkening at 205-210°.

Acetylation of tetra N-methyl holarrhimine —A mixture of 0.1 g. substance, 0.2 g. sodium acetate (freshly dehydrated) and 0.5 c.c. acetic anhydride was heated in a water-bath for 3 hours. On working up the straw-coloured reaction mixture and liberating the base with caustic soda, it came out as a sticky semisolid which was taken up in ether and dried over sodium sulphate. On removal of the solvent a crystalline residue was left, which when washed with the least amount of cold acetone and dried formed a white crystalline powder softening at 134°, melting sharply at 139-40° to a straw-coloured liquid (yield, 0.08 g.). In contrast to the un-acetylated base it is readily soluble in ether and petroleum ether, slightly less so in acetone and crystallises on evaporation of the solvents in aggregates of stout rods. (Found: C, 76.02; H, 10.04; $C_{25}H_{43}ON_2 \cdot CO \cdot CH_3$ requires C, 75.32; H, 10.69, $C_{25}H_{44}ON_2$ requires C, 77.3; H, 11.3 per cent)

—*hydrochloride* came out on adding ethereal hydrochloric acid to the ethereal solution of the base as an oil, which when washed repeatedly with ether and evacuated formed a white hygroscopic powder. It appeared to give off water with frothing from 230° onwards forming a porous skeleton which abruptly melted with darkening and frothing at 273°.

—*picrate* was obtained on adding aqueous picric acid to an aqueous solution of the hydrochloride. It forms a brilliant yellow crystalline powder fairly soluble in alcohol and acetone, sparingly in water. After drying in air it appeared to give off water 105° onwards, gradually stuck to the sides, and melted down at 160° to an orange-coloured treacle which frothed up with blackening at 202-5°.

Salimuzzaman Siddiqui. Proc. Ind. Acad. Sci., A, vol. III, Pl XVII.



Tetra N-methyl holarchumme

THE ALKALOIDS OF HOLARRHENA ANTI-DYSENTERICA.

Part V. Studies in Holarrhimine.

BY SALIMUZZAMAN SIDDIQUI

AND

RAFAT HUSAIN SIDDIQUI,

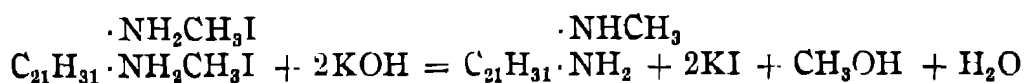
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THE relation between conarrhimine, $C_{21}H_{31} \cdot \begin{smallmatrix} \cdot NH \\ \cdot NH \end{smallmatrix}$ and holarrhimine, $C_{21}H_{31} \cdot \begin{smallmatrix} \cdot NH_2 \\ \cdot OH \end{smallmatrix}$, suggested in the earlier communication¹ made it desirable to

extend the studies in holarrhimine beyond the position arrived at in Part IV, wherein tetra N methyl holarrhimine and its benzoyl and acetyl derivatives were characterised, and the action of nitrous acid on holarrhimine was qualitatively observed to yield a nitrogen-free, oily product. The present paper gives the results of studies in methylation, benzylation and acetylation of holarrhimine.

On treatment of holarrhimine with 4 mols of benzoyl chloride, di- and tri- benzoyl derivatives were formed, and with large excess of acetic anhydride and sodium acetate a tri-acetyl derivative was obtained. With 2 mols of methyl iodide, holarrhimine dimethyliodide was obtained which, however, unexpectedly yielded monomethyl holarrhimine on treatment with caustic soda or silver hydroxide, probably as a result of splitting of one molecule of methyl alcohol in the process of liberation of the base



The analysis of the non-nitrogenous product, obtained through the action of nitrous acid on holarrhimine and expected to correspond to the formula $C_{21}H_{34}O_3$ gave too high carbon value for this formula. This may probably be due to its slight impurity with a product resulting from a subsequent splitting of a molecule of water. As the substance could not so far be obtained in a pure condition, its description is not included in the practical. It may,

¹ *Proc Ind. Acad. Sci.*, 1935, 2, 426.

however, he stated here that this product as well as holarrhimine showed, like conessine, the presence of only one double bond, on titration with bromine. But in each case the brominated products gave on isolation and analysis too low bromine value due probably to a subsequent partial splitting of one HBr, as has been noted in the case of conessine ²

It was intended to study holarrhimine more closely but as one of us (R S.) had to leave for foreign studies, these joint investigations had to be brought to an abrupt close

2 Experimental

Benzoylation of holarrhimine: Tri-benzoyl holarrhimine—To a solution of holarrhimine (0.5 g. 1 mol) in 3 c.c. pyridine was added benzoyl chloride (0.85 g. 4 mols) with ice cooling and stirring and the reaction mixture was left well corked at room temperature for two hours. On dilution with water a non-basic crystalline mass separated out which was well washed with water and acetic acid to remove any unchanged base. On recrystallisation from chloroform it formed snow-white hexagonal rods m.p. 269-70° (yield, 0.85 g.). It is soluble in ethyl acetate, alcohol, chloroform and insoluble in ether and petroleum ether (Found: C, 78.45, 78.20; H, 7.60, 7.64; N, 4.57; $C_{21}H_{33}ON_2 (CO C_6H_5)_3$ requires C, 78.26, H, 7.45; N, 4.35 per cent.).

Di-benzoyl holarrhimine—The mother liquor from tri-benzoyl holarrhimine gave on removal of the solvent the dibenzoyl product as a semi crystalline white powder (0.10 g.) which was easily soluble in ether, petroleum ether and other organic solvents and frothed up at 115° (Found: C, 77.74; H, 7.77; N, 4.64; $C_{21}H_{34}ON_2 (CO.C_6H_5)_2$ requires C, 77.77; H, 8.14; N, 5.14 per cent.)

Acetylation of holarrhimine: Tri-acetyl holarrhimine.—An intimate mixture of holarrhimine (0.5 g.), anhydrous sodium acetate (2 g.) and acetic anhydride (2 c.c.) was heated on the water-bath for two hours. On dilution and further heating on the water-bath a non-basic mass was obtained, which crystallised out of alcohol and ethyl acetate in clusters of spindle-shaped needles melting at 240-41°. On recrystallisation from methyl alcohol and acetone it formed snow-white spindle-shaped needles melting at 249-50° (yield, 0.75 g.). It is soluble in benzene, chloroform, acetone, alcohol, and insoluble in ethyl acetate, ether and petroleum ether. On dehydration at 100° *in vacuo* over P_2O_5 it lost 3.7 per cent. water of crystallisation. $C_{21}H_{33}ON_2 (CO C_6H_5)_3 + H_2O$ requires H_2O , 3.1 per cent. (Found: C, 69.87, 69.90; H, 9.34, 9.20; N, 6.00; $C_{21}H_{33}ON_2 (CO.C_6H_5)_3$ requires C, 70.74; H, 9.17; N, 6.30 per cent.).

² *Arch. Pharm.*, 1918, 256, 57.

Bromination of holarrhimine: *Di-bromo holarrhimine*—0.2 g. holarrhimine dissolved in dry chloroform was titrated against bromine in dry chloroform solution with ice cooling, when it took up 0.10 g bromine (calculated for one double bond 0.10 g.) The titration was followed by means of potassium iodide starch paper. After titration the bromo compound was completely precipitated by adding ether to the mixture. Well washed with ether it melted at 290-95°. On liberation with caustic soda from its acetic acid solution, the bromo base melted at 226-28° (decomp.). It was soluble in alcohol and water and insoluble in chloroform, acetone, ethyl acetate, ether and petroleum ether (Found C, 51.99; H, 7.98; N, 5.43; Br, 28.32; $C_{21}H_{36}ON_2Br_2$ requires C, 51.20, H, 7.33, N, 5.69, Br, 32.5 per cent.).

Methylation of holarrhimine with methyl iodide: *Di-methyl holarrhimine hydroiodide*—To a solution of holarrhimine (1 g) in dry chloroform was added a chloroformic solution of methyl iodide (1 g. 2.3 mols) and the reaction mixture kept overnight at room temperature when a crystalline product separated out, m.p. 276°. On recrystallisation out of alcohol it melted at 278°. It was soluble in warm alcohol and water, insoluble in acetone, ethyl acetate and chloroform (Found. C, 44.84; H, 7.13, N, 4.54, CH_3 , 5.93, $C_{21}H_{36}ON_2(CH_3I)_2$ requires C, 44.80, H, 6.82; N, 4.55, CH_3 for 2 N- CH_3 , 4.87 per cent.).

Methyl holarrhimine—The aqueous solution of the hydroiodide gave on liberation with ammonia or caustic soda a very small quantity of a white precipitate which after crystallisation from methyl alcohol and ether formed snow-white needles melting at 170° (Found after dehydration at 100° *in vacuo*: C, 74.92, H, 10.82, N, 8.33, $C_{22}H_{38}ON_2$ requires C, 76.30; H, 10.98, N, 8.09; per cent.). A more quantitative yield was obtained on liberation of the base with freshly precipitated silver hydroxide. The base, thereby obtained, also melted at 169-70° and gave no depression with the base liberated with caustic soda. It showed the presence of only one N- CH_3 after Herzig and Meyer (Found: CH_3 , 3.91; $C_{22}H_{38}ON_2$ requires for 1 N- CH_3 , CH_3 , 4.32 per cent.) (Found in air dried substance: C, 71.9; H, 10.7; N, 7.1; $C_{22}H_{38}ON_2 + H_2O$ requires C, 72.5; H, 11.0; N, 7.7; after dehydrating at 100° C, 75.0, 75.1; H, 11.0, 11.2; N, 7.8, 7.8; $C_{22}H_{38}ON_2$ requires C, 76.3; H, 11.0, N, 8.1 per cent.). The dehydration at 100° was apparently not complete.

—*hydrochloride* was obtained by adding ethereal hydrochloric acid to a solution of the base in methyl alcohol and acetone as a white semi-crystalline powder which melted at 266° (decomp.) and was soluble in alcohol and water (Found: Cl, 16.16; $C_{22}H_{38}ON_2 \cdot 2HCl$ requires Cl, 16.95 per cent.).

—*chloroplatinate* was obtained as a golden yellow powder, when a 10 per cent solution of platinic chloride was added to an aqueous solution of the hydrochloride. It was soluble in alcohol and water and melted at 245° with blackening and decomposition (Found : Pt, 25.6 ; $(C_{22}H_{38}ON_2 \cdot 2HCl) \cdot PtCl_4$ requires Pt, 25.8 per cent).

—*picrate* was prepared by adding ethereal picric acid to a solution of the base in methyl alcohol and acetone. It crystallises out of alcohol and water in tufts of lemon-yellow needles, sparingly soluble in hot water, fairly soluble in alcohol and melting at 205° .

DERIVATIVES OF SALICYLIC ACID—PART X.

Stability of the Sulphonic Acid Group in the 4-Sulphosalicylic Acid.

Part II.—Bromination of 4-Sulphosalicylic Acid.

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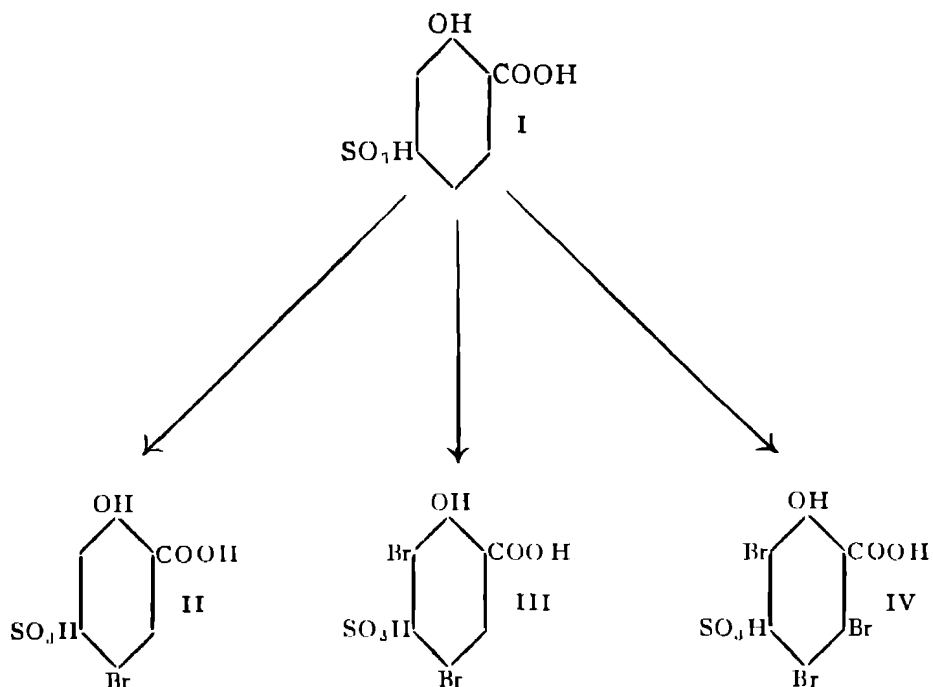
IN continuation of Part I "Nitration of 4-sulphosalicylic acid" * the action of bromine on 4-sulphosalicylic acid has been studied.

The action of halogens on sulphonic acids has been studied by Kelce¹ who has obtained tetrachloro-cymene from cymene sulphonic acid; by Meyer² who has obtained *p*-dichlorobenzene from *p*-chlorobenzenesulphonic acid; by Sudborough and Lakhumalani³ who obtained aminochlorobenzene from aminobenzenesulphonic acid. The same reaction has also been studied with regard to 5-sulphosalicylic acid. It has been found that the sulphonic acid group is readily substituted by halogens, if the reaction is carried further phenols are obtained by the substitution of the -COOH group by halogens. Rusiklal Datta and Mitter⁴ have shown that on chlorination 5-sulphosalicylic acid gives 3,5-dichlorosalicylic acid. Datta and Bhounik⁵ obtained 2:4:6-tribromophenol by the action of bromine on the same sulpho acid. F. Sakellarios⁶ has converted potassium-hydrogen-3-nitro-5-sulphosalicylate by the action of bromine into 4:6-dibromo-2-nitrophenol.

With a view to study the stability of the sulphonic acid group in 4-sulphosalicylic acid (I), it was treated with bromine when bromosulphosalicylic acid (II), dibromosulphosalicylic acid (III) and tribromosulphosalicylic acid (IV) were obtained. It is interesting to note that even with excess of bromine the reaction does not proceed further and neither the -SO₃H nor -COOH is eliminated.

In view of the combined directing influences of -OH and -COOH groups in salicylic acid and also the preference for the position -5 over that of -3, the constitution of the above described acids follow, as shown in the diagram.

* *Proc. Ind. Acad. Sci.*, 1936, 3, 236.



The stability of both the $-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups and the absence of a tribromophenol-*m*-sulphonic acid similar to trinitrophenol-*m*-sulphonic acid† finds an easy explanation in the combination of the directing influences of $-\text{OH}$ and $-\text{COOH}$ on the one hand and $-\text{SO}_3\text{H}$ and Br on the other in the same molecule.

The first bromine enters position -5 and gives (II) in obedience to the combined influence of $-\text{OH}$ and $-\text{COOH}$ in spite of the opposing influence of $-\text{SO}_3\text{H}$. Similarly the second bromine enters the position -3 and gives (III). But when (III) is now further brominated, the combined influences of $-\text{SO}_3\text{H}$ (*m*), $-\text{Br}$ (*o*), and Br (*p*), become stronger than that of the $-\text{OH}$ (*o*) and thus the third bromine enters position -6 and does not eliminate the $-\text{COOH}$ group. Thus for the sum of the directing influences we have, $\text{OH} + \text{COOH} > \text{Br} + \text{SO}_3\text{H}$ and $\text{Br} + \text{SO}_3\text{H} + \text{Br} > \text{OH} + \text{the resistance from } -\text{COOH}$.

The stability of the $-\text{SO}_3\text{H}$ group depends on where it is placed in the molecule. If it is subjected to stronger directing influences as with 3-sulphosalicylic acid or 5-sulphosalicylic acid it is easily substituted either by $-\text{NO}_2$ group or by bromine, but if it is outside this influence as with 4-sulphosalicylic acid its substitution by these groups becomes impossible. Similarly the $-\text{COOH}$ group which is eliminated in nitration is completely protected in bromination.

† *Proc. Ind. Acad. Sci.*, 1936, 3, 236.

*Experimental.**Bromination of 4-sulphosalicylic acid .—*

4-Sulpho-5-bromosalicylic acid.—Bromine (10 g) vapour was passed into 4-sulphosalicylic acid (13 g) dissolved in water (50 c c) and the mixture kept overnight. The solid obtained on evaporation was pressed on a porous tile and dried over sodium hydroxide to remove hydrobromic acid. It crystallises from a little water in needles with four molecules of water , m p. 210°. It is not hygroscopic. (Found : Equivalent, 181.8 ; S, 8.6 , Br, 22.1 ; H₂O, 19.4. C₇H₅O₆SBr, 4H₂O requires equivalent, 184.5 ; S, 8.7 , Br, 21.6 , H₂O, 19.5 per cent.)

Neutral barium-4-sulpho-5-bromosalicylate—which was obtained by neutralising the acid with barium carbonate, crystallised from water as grey white powder, with four molecules of water of which three can be driven out at 200° under reduced pressure. It turns pale yellow on heating (Found : Ba, 27.3 , H₂O, 10.8 , C₇H₃O₆SBrBa, 4H₂O requires Ba, 27.2 , H₂O, 14.3 per cent and C₇H₃O₆SBrBa, 3H₂O requires Ba, 28.2 , H₂O, 11.1 per cent)

Acid potassium-4-sulpho-5-bromo-salicylate.—The acid was neutralised and strongly acidified with hydrochloric acid. On concentration a salt separated which crystallised from water in white needles (Found : K, 11.7 , C₇H₄O₆SBrK requires K, 11.6 per cent)

4-Sulpho-3 : 5-dibromo-salicylic acid—was prepared as described for the monobromo acid using twice the quantity of bromine. It was more soluble in water than the mono-bromo-acid and crystallised in long white needles with m p 83°. It was hygroscopic and so it was kept over CaCl₂ for analysis (Found : S, 7.0 ; Br, 35.6 , H₂O, 15.9 , equivalent, 222.7 ; C₇H₄O₆SBr₂, 4H₂O requires S, 7.2 , Br, 35.7 , H₂O, 16.1 per cent ; equivalent, 224.0)

Acid potassium-4-sulpho-3 : 5-dibromo-salicylates—was obtained by acidifying a solution of the neutral salt. It crystallised from water in white needles. (Found : K, 9.5 ; C₇H₃O₆SBr₂K requires K, 9.4 per cent.)

Neutral barium-4-sulpho-3 : 5-dibromo-salicylate—was prepared by neutralising the acid with barium carbonate. It crystallised from water as microscopic grey needles, with one molecule of water. (Found : Ba, 26.2 ; H₂O, 3.2 ; C₇H₂O₆SBr₂Ba, H₂O requires Ba, 26.0 ; H₂O, 3.4 per cent)

4-Sulpho-3 : 5 : 6-tribromo-salicylic acid was prepared as described for the monobromo acid using three times the quantity of bromine. The solid obtained on concentration contained hydrobromic acid which was removed under reduced pressure at 100°. The residue, after pressing on a porous tile and drying over alkali, crystallised from water in needles, m.p 115°.

(Found : S, 7.2 ; Br, 53.0 ; equivalent, 227.5 ; $C_7H_3O_6SBr_3$ requires S, 7.0 ; Br, 52.7 per cent ; equivalent, 227.4)

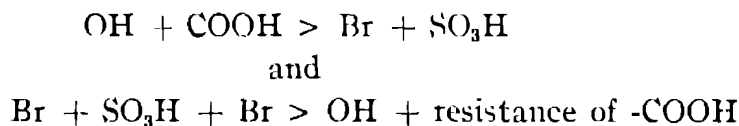
Neutral barium-4-sulpho-3 : 5 : 6-tribromo-salicylate—was obtained by neutralising the acid with barium carbonate. It crystallised from water in microscopic grey needles, with two molecules of water (Found : Ba, 22.0 ; H_2O , 5.5 ; $C_7HO_6SBr_3Ba \cdot 2 H_2O$ requires Ba, 21.9 ; H_2O , 5.7 per cent.)

One of the authors (N.W H) desires to thank the Research Grant Committee of the University of Bombay for a grant, which defrayed a part of the expenses of this investigation. The authors also feel indebted to Dr T. S. Wheeler for his lively interest in the work

Summary

4-Sulphosalicylic acid gave on bromination (I) 4-sulpho-5-bromosalicylic acid, (II) 4-sulpho-3 : 5-dibromosalicylic acid, (III) 4-sulpho-3 : 5 : 6 : tribromosalicylic acid

The experimental results indicate that the relation of the directing influences is as follows :—



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THE TRACKS OF THE α -PARTICLES OF THORIUM AND ITS PRODUCTS.

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AND

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It has been known for many years¹ that α -particles can be recorded by allowing them to pass through a photographic emulsion. The emulsion consists of numerous grains of silver bromide, embedded in gelatine, and an α -particle traversing the emulsion will pass through those grains which lie on its path. These grains are affected by the α -particle, in much the same way as they are affected by light in the ordinary photographic process. When the plate is developed, these grains are accordingly reduced by the chemical action of the developer, and become grains of solid silver. Unaffected grains are dissolved out by a solution of hypo. In the developed plate, therefore, the paths of α -particles which have passed through the emulsion are visible as rows of black grains. A high magnification is necessary for observing these tracks.

More recently the technique has been improved, and the method has been applied in several investigations.^{2,3,4,5,6} Special plates are used, coated with the new Ilford "R" emulsion. This emulsion is specially suitable for recording α -particle tracks, and was originally prepared in the Ilford laboratories for this purpose.⁷ The grains are very small, the mean diameter being only $0.3\ \mu$. The stopping power of the emulsion for α -particles is about 1400 times greater than that of air, one cm. path in air is equivalent to $7\ \mu$ in the emulsion, and the mean number of grains in a path of this length is five. The number of grains corresponding to a given length of path is naturally subject to considerable variations.

In order to record the tracks of the α -particles emitted by thorium and its products, the following method was used. A weak solution of thorium nitrate was prepared, and a plate was placed in the solution for about twenty minutes. The plate was then removed and dried, all the operations, of course, being carried out in complete darkness in order to avoid fogging.

When the plate dries, the solute remains in the gelatine, so that thorium atoms are distributed uniformly through the emulsion. These atoms remain in practically fixed positions during the progress of the experiment. After an interval of three days, the plate was developed and fixed in the normal manner, and after drying was examined microscopically. (For this purpose we use a fluorite dry objective corrected for use with uncovered objects, N.A. = 0.90, and a total magnification of $900\times$. It is impracticable to use an oil-immersion objective.)

Many more tracks are observed than can be ascribed to thorium alone, since all the members of the thorium series are present. In the complete transformation from thorium to thorium D, an atom emits six α -particles. The series is well known, and the relevant data are given in the following table :

Element	Type of Disintegration	Range of α -particle in cms air at 18°C.	Decay constant	Half-value period
Thorium	α	2.93	$1.33 \times 10^{-10} \text{ sec.}^{-1}$	1.65×10^{10} years
Mesothorium I	β		3.28×10^{-9}	6.7 years
Mesothorium II	β		3.14×10^{-5}	6.1 hours
Radiothorium	α	4.05	1.16×10^{-8}	1.9 years
Thorium X	α	4.40	2.20×10^{-6}	3.6 days
Thorium Emanation	α	5.11	1.27×10^{-2}	54.5 secs.
Thorium A	α	5.74	4.78	0.14 secs.
Thorium B	β		1.82×10^{-5}	10.6 hours
Thorium C	α & β	4.82	1.91×10^{-4}	60.5 mins.
Thorium C'	α	8.70	ca. 10^{11}	very short
Thorium C''	β		3.61×10^{-3}	3.2 mins.
Thorium D	stable			

The series branches at Th. C, which disintegrates *either* with the emission of an α -particle, to give Th. C'', *or* with the emission of a β -particle, to give Th. C'. Thus the α -particles of Th. C and Th. C' are alternative; in the

course of its disintegration an atom emits either one or the other, but not both.

Let us suppose that a particular atom of thorium in the emulsion emits its α -particle. The chance that the same atom will emit a further α -particle during the period of the experiment is very small. Indeed it will be several years before any appreciable fraction of the atoms have reached the stage of emitting the next α -particle, since the half-value periods of MsTh. I and RdTh. are large. The tracks should therefore occur singly, and several tracks radiating from a single point are not to be expected. Many such single tracks due to the α -particles of thorium are actually observed.

Radiothorium is an isotope of thorium, and is probably present in the original solution in the equilibrium amount. This element is thus introduced into the emulsion with the thorium, and the amount of RdTh. present will not vary appreciably during the period of the experiment. We can therefore calculate the amounts of the subsequent products which are present at any later time. Let the decay constants of a series of consecutive elements be denoted by $\lambda_1, \lambda_2, \lambda_3, \dots$ and suppose that the first element is the only one which is present initially. Then the amount of the n th element at the time t is given by the expression

$$N(t) = c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} + \dots + c_n e^{-\lambda_n t}$$

where

$$c_1 = N_0 \cdot \lambda_1 \lambda_2 \dots \lambda_{n-1} / (\lambda_2 - \lambda_1) (\lambda_3 - \lambda_1) \dots (\lambda_n - \lambda_1)$$

$$c_2 = N_0 \cdot \lambda_1 \lambda_2 \dots \lambda_{n-1} / (\lambda_1 - \lambda_2) (\lambda_3 - \lambda_2) \dots (\lambda_n - \lambda_2)$$

..... etc.

N_0 = number of atoms present initially.

We are chiefly interested in the amounts of the elements Th. X, Th. B, and Th. D which are present in the emulsion, since the short-lived elements will be present only in infinitesimal amounts. Before an atom of Th. X can be formed, its parent RdTh. atom must have emitted an α -particle, so that every Th. X atom present should be the point of origin of a single track in the emulsion. Before an atom of Th. B can be formed, four α -particles must be emitted, and therefore every Th. B atom present should be at the point of origin of four tracks. Similarly, five tracks should radiate from every Th. D atom present.

If the calculation be made, for example, with $t = 3 \cdot 10^5$ seconds ($= 3\frac{1}{2}$ days, the approximate exposure in the experiments), we find the relative numbers of atoms are as follows:

Th. X (origin of a single track)	25
Th. B (centre of a "star" of four tracks)	2.6
Th. D (centre of a "star" of five tracks)	31

In the original solution, some of the later products of disintegration (Th X and Th B) are already present, though not necessarily in equilibrium amount. These will give some additional tracks. The transition Th. X \rightarrow Th. B will produce a "star" of three tracks, the transition Th. X \rightarrow Th. D will produce a "star" of four tracks, and the transition Th. B \rightarrow Th. D will give a single track, either long (8.7 cms) or short (4.8 cms)

It is clear, then, that a plate should show, on examination :

- (a) Single tracks corresponding to the α -particles of Th.
- (b) A number of "stars" consisting of five tracks radiating from a point
- (c) A somewhat smaller number of single tracks corresponding to the α -particles of RdTh
- (d) A few "stars" of three or four tracks.
- (e) A few single tracks corresponding to the α -particles of Th. C and Th. C'

The observations confirm these conclusions. It is not possible, however, to check the relative numbers of single tracks and "stars", except very roughly. The reason for this is that the atoms are situated at all depths in the emulsion, and the α -particles are emitted in all directions. Only tracks lying in or near the horizontal plane are suitable for measurement, and as many of the α -particles pass out of the emulsion altogether, their tracks are incomplete. This will be easily understood when it is remembered that the thickness of the emulsion does not exceed 14μ , the equivalent of 2 cms of air.

The identification of individual tracks presents great difficulty. It has been pointed out previously that the tracks corresponding to α -particles of a given energy show considerable variations in length, and a critical discussion of these variations has been given⁶. If a large number of tracks, produced by α -particles of the same energy, are measured, a frequency curve of the measurements can be constructed. From this curve it is possible to obtain a quantity known as the "extrapolated length" of the tracks, which can be determined with some accuracy, and which is strictly proportional to the range in air of the same particles. From the measurement of a *single* track, however, there is a large uncertainty in the determination of the corresponding range in air. In a "star" of five tracks, usually only the long track corresponding to the Th.C' α -particle (8.7 cms) can be identified with certainty. The ranges of the other α -particles do not differ sufficiently for the tracks to be distinguished unambiguously.

Many hundreds of "stars" have been observed. In order to obtain a photomicrograph of a "star", all five tracks must be approximately in the horizontal plane, and the central point must not be too near the surface of the emulsion, or some tracks may fail to be recorded. The probability that an individual track will lie sufficiently near the horizontal plane for this purpose is certainly not more than $\frac{1}{3}$, and the probability that all the five tracks will be complete and well-placed for photomicrography is probably not more than $1/50,000$. One can therefore hardly expect to find a perfect specimen. After some weeks of careful searching two "stars" have been found, however, in which the conditions are nearly fulfilled. These are shown in the diagram (Figs. 1 and 2), which may be compared with the photomicrographs (Figs. 3 and 4). Measurements of the tracks give the following results:

Track	Length in μ	Calculated range in cms. of air	Remarks
Figs. 1 & 3—			
<i>a</i>	57	8.51	α -particle of Th. C'
<i>b</i>	28.5	4.26	
<i>c</i>	26.3	3.93	
<i>d</i>	track incomplete
<i>e</i>	28.5	1.26	
Figs. 2 & 4—			
<i>a</i>	56	8.36	α -particle of Th. C'
<i>b</i>	34	5.08	? Th. Em. or Th. A
<i>c</i>	29	4.33	
<i>d</i>	6.3	..	track incomplete
<i>e</i>	track out of focus

The chief interest of the present observations lies in the fact that we have the whole history of an isolated radioactive atom, recorded as a "star" in the emulsion. Other methods of studying radioactive transformations, on the other hand, give only the "average history" of a large number of atoms, or else, as in the Wilson chamber, give a record of the transformations occurring during a very small interval of time.

There is some evidence that an atom may occasionally diffuse through the emulsion for a perceptible distance during the progress of the experiment. Occasionally instances are found in which the five tracks belonging, apparently, to the same "star", do not diverge from exactly the same origin. This suggests that the atom has moved, say, in the time between the emission of the first α -particle and the emission of the last four. The extent of this apparent movement is not more than three or four μ . This is a point, however, upon which it is difficult to come to any certain conclusion, for the

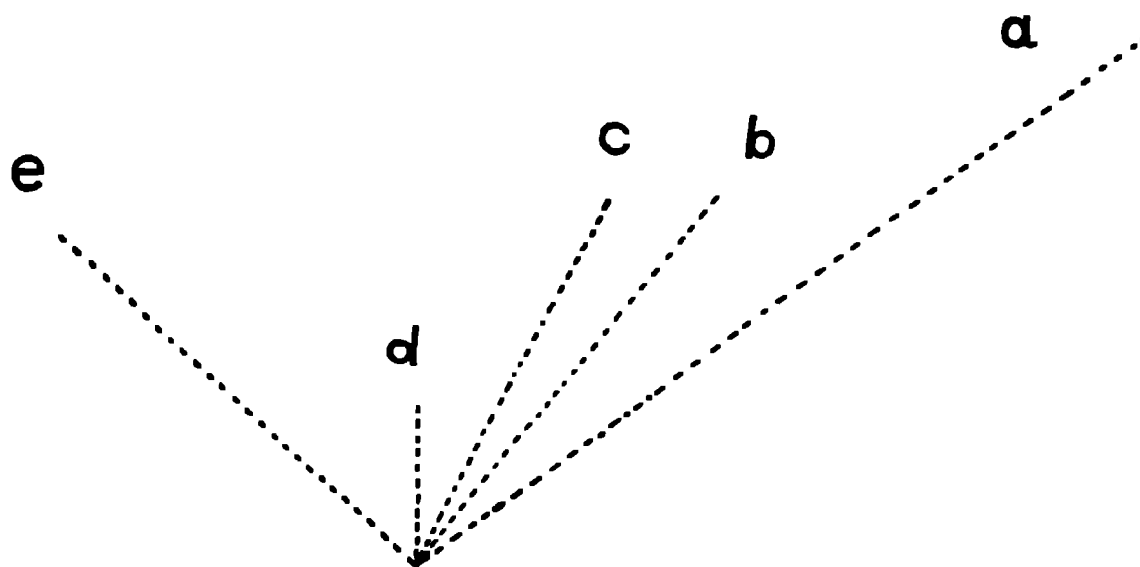


FIG. 1.

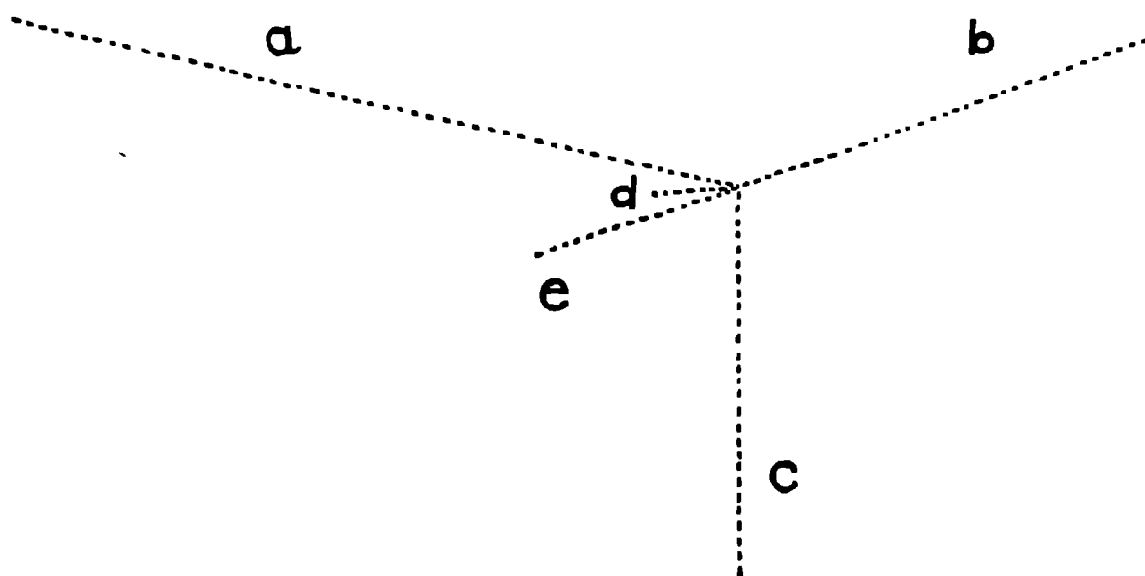


FIG. 2.

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and V. D. Dabholkar.

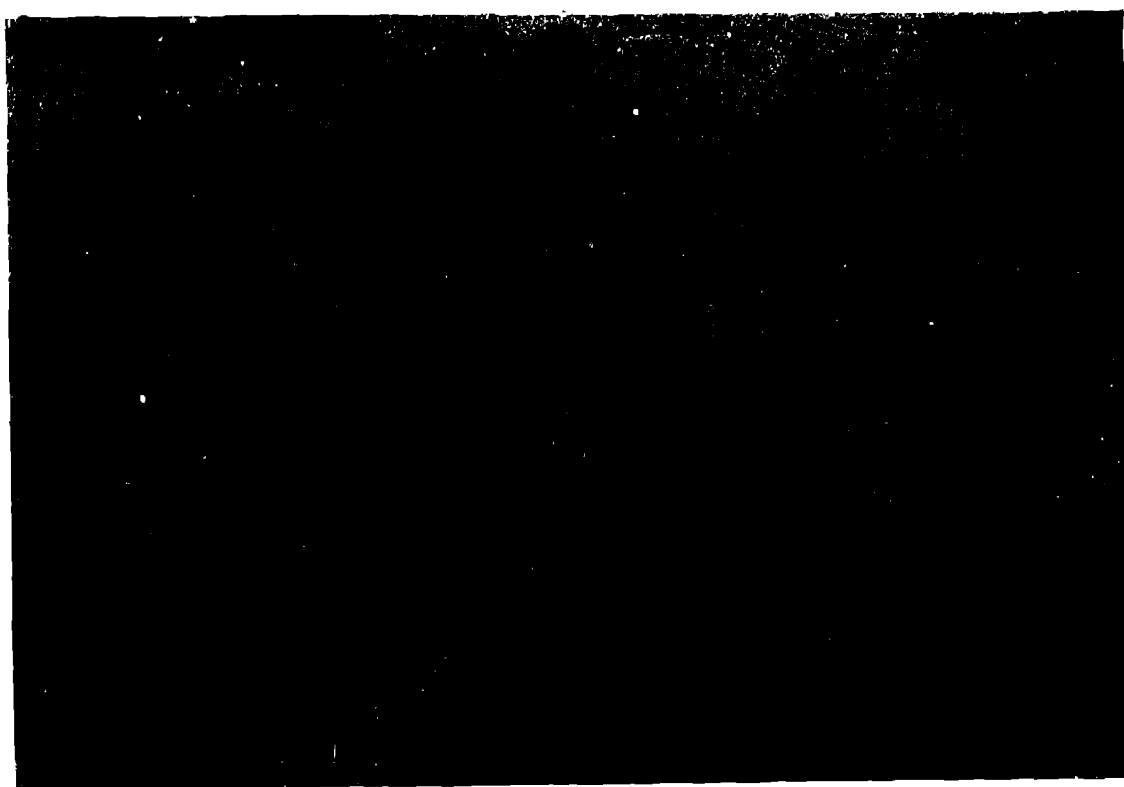


FIG. 3. Magnification $\times 1135$

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Proc. Ind. Acad. Sci., A, vol. III, Pl. XIX.

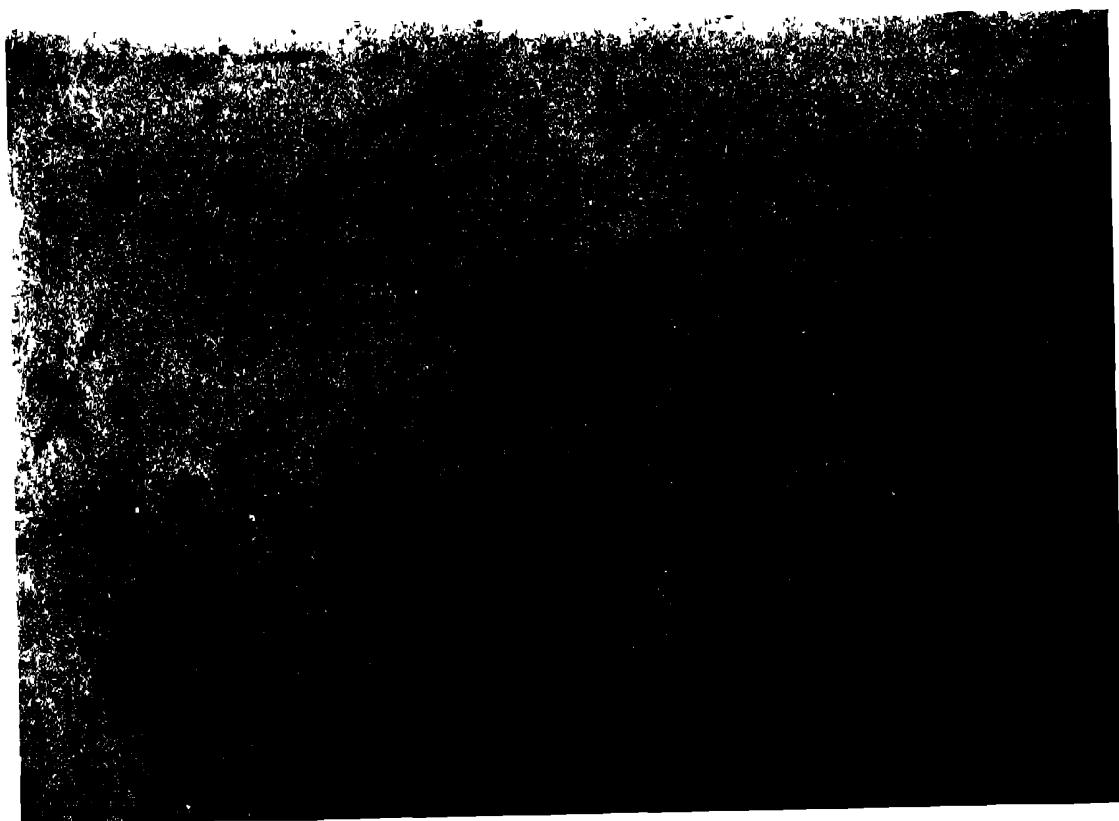


FIG. 1. Magnification $\times 1135$

tracks are not continuous lines, and the path of an α -particle does not necessarily pass through the centre of a grain. If an α -particle merely grazes the edge of a grain, this grain appears, to the eye, somewhat displaced. It is therefore very difficult to be quite sure that the tracks do not, in reality, diverge from the same point. Furthermore the effect might be simulated by the slight scattering of an α -particle after it had travelled a short distance through the emulsion; and there is always the possibility that the displaced track is really an independent single track, not connected with the "star". Taking these possibilities into account, one is nevertheless led to the view that an appreciable displacement of the atoms does actually occur, though it is not sufficiently definite to lead to any quantitative information on the diffusion of heavy atoms in gelatine.

A noteworthy point is that "stars" of more than five tracks are very infrequent, indicating that the molecules of radiothorium nitrate are deposited singly in the emulsion, and do not tend to associate in groups. Very infrequently a "star" of perhaps a hundred tracks may be found, which must be due to a group of many molecules. Possibly under certain circumstances there is a kind of incipient crystallisation in the gelatine. This, however, is quite exceptional, and as a rule is not found.

In conclusion, we wish to express our thanks to Lord Rutherford for his continued interest in these experiments.

Summary.

The tracks of the α -particles from members of the thorium series have been recorded in a photographic emulsion, by the use of a technique previously developed. Radiothorium atoms introduced into the emulsion disintegrate *in situ*, emitting five α -particles in succession. In this way "stars" are produced, consisting of five tracks radiating from a point, of which a discussion is given. Photomicrographs of two "stars" are reproduced.

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ON THE THEORY OF PRESSURE BROADENING OF SPECTRAL LINES.

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Introduction

THE asymmetric broadening and shift of spectral lines under foreign gas pressure are ascribed to perturbations of the energy levels of the excited atoms, due partially to their coupling with the same set of virtual oscillators of the foreign gas, which determine its dispersion. These "dispersion forces" have been first considered in this connection by Margenau.¹ A shorter and more general treatment of these forces is possible, which yields a simple relation between the refractive index of the perturbing gas and the red shift produced by these interactions (Section I.)

Width and violet shift may be partially due to coupling interactions of a more general type, which would depend to some extent upon the alteration of the relative positions of perturbing and radiating atoms. (Section II.)

The equations describing varying interactions can be solved by successive approximations. This method allows a simultaneous treatment of impact broadening and statistical distribution of the frequency displacements, which have been usually treated as formally distinct (v. e. g^2). (Section III.)

I.

We base our considerations on the set of equations

$$(1) \quad \ddot{q}_i + 2x_i\dot{q}_i + \omega_i^2 q_i + \sum_j (j \neq i) (a_{ij}\ddot{q}_j + 2k_{ij}\dot{q}_j + b_{ij}q_j) = F(t)$$

where x_i is the transition probability for the i -th oscillator in case of vanishing interaction, ω_i its characteristic frequency and $F(t)$ an external force. Holtsmark's,³ Mensing's^{4,5} and Frenkel's⁶ theory of resonance broadening is based upon equations of the same form containing only the coupling coefficients b_{ij} . A possible physical interpretation of the coupling forces $a\ddot{q}$ and $k\dot{q}$, which are introduced at present hypothetically, will be discussed in Section II. All the coefficients $a_{ij} = a_{ji}$, etc., since equations (1) can be derived from an energy function.

The electric field strength due to the dipole eq_j at the place of the i -th dipole is

$$\begin{aligned} |\vec{E}| &= \frac{eq_j}{r_{ij}^3} \cdot \sqrt{(1 - 3 \cos^2 \theta_{ij})^2 + 9 \cos^2 \theta_{ij} \sin^2 \theta_{ij}} \\ &= \frac{eq_j}{r_{ij}^3} \sqrt{1 + 3 \cos^2 \theta_{ij}} \end{aligned}$$

where θ_{ij} is the angle between the axis of the j -th dipole and the line joining it with the i -th dipole, r_{ij} . Terms of higher order in $1/r$ are omitted under the assumption that

$$(2) \quad r_{ij} \gg q_j$$

This electric field strength is represented in (1) by the term $b_{ij}q_j$, which becomes identical with $|\vec{E}|$, when it is multiplied by m/e , m and e being the mass and charge of the electron. We have thus

$$(3) \quad b_{ij} = \frac{e^2}{r_{ij}^3 m} \times \sqrt{3 \cos^2 \theta_{ij} + 1}$$

We consider now the interaction of one excited atom, denoted by the index 1, with perturbing, unexcited molecules of the foreign gas. If $\omega_1 \neq \omega_j$ and

$$(4) \quad |a_{ij}| \ll 1, |k_{ij}| \ll \omega_1, |b_{ij}| \ll \omega_1^2$$

and if, further, all the coupling coefficients can be considered as constant, we easily obtain (v. Courant-Hilbert, *Meth. der math. Phys.*, 1924, p. 231) the additional transition probability

$$(5) \quad x' = \sum_{j=2}^n \frac{2k_{ij} \omega_1^2 (a_{1j} - b_{1j}/\omega_1^2)}{\omega_j^2 - \omega_1^2}$$

and the frequency displacement

$$(6) \quad \Delta\omega = -\frac{1}{2} \omega_1 \sum_{j=2}^n \frac{(a_{1j} - b_{1j}/\omega_1^2)^2 \omega_1^2 - k_{1j}^2}{\omega_j^2 - \omega_1^2}$$

terms of higher order in the coupling coefficients being omitted. Since $\omega_j > \omega_1$, if ω_j are the characteristic frequencies of the virtual dispersion oscillators of the foreign gas, we have red shift for

$$(7) \quad |a_{1j} - b_{1j}/\omega_1^2| \omega_1 > |k_{1j}|$$

and violet shift for

$$(7') \quad |a_{1j} - b_{1j}/\omega_1^2| \omega_1 < |k_{1j}|$$

The red shift due to the electrostatic coupling (3) is

$$(8) \quad \Delta\omega = -\frac{1}{2} \cdot \frac{e^4}{m^2} \cdot \frac{1}{\omega_1} \sum_{j=2}^n \cdot \frac{1}{r_{ij}^6} \cdot \frac{1}{\omega_j^2 - \omega_1^2} (3 \cos^2 \theta_{1j} + 1)$$

If all the perturbing molecules are identical ($\omega_1 = \omega_2$ for $j \neq 1$) and equally distributed, we obtain the average red shift by replacing for the sum the corresponding integral from R_0 , the distance of mean closest approach between the excited atom and its perturbers, to infinity.

$$\Delta\omega = -\frac{1}{2} \frac{e^4}{\omega_1 m^2} \frac{N}{\omega_2^2 - \omega_1^2} \int_{R_0}^{\infty} \int_0^{\pi} \int_0^{2\pi} \frac{1}{r^4} dr \cdot (3 \cos^2 \theta + 1) \sin \theta \cdot d\theta \cdot d\phi$$

where N is the number of foreign gas molecules per unit volume. Evaluating this integral we obtain

$$(9) \quad \Delta\omega = -\frac{4\pi}{3} \cdot \frac{e^4}{\omega_1 m^2} \cdot \frac{N}{\omega_2^2 - \omega_1^2} \cdot \frac{1}{R_0^3}$$

Under the same assumptions, the classical theory of dispersion yields for the refractive index the expression

$$\mu - 1 = 2\pi \cdot \frac{e^2}{m} \cdot \frac{N}{\omega_2^2 - \omega_1^2}$$

Combining it with (9), we obtain

$$(10) \quad \Delta\omega = -\frac{2}{3} \frac{e^2}{\omega_1 m} \cdot \frac{1}{R_0^3} (\mu - 1)$$

If more than one type of virtual oscillators are considered, $N/(\omega_2^2 - \omega_1^2)$ has to be replaced by the appropriate sum. (10) is also valid in this case.

The wave-length shift, corresponding to (10), is

$$(11) \quad \Delta\lambda = \frac{4\pi e^2}{3mc^2} \left(\frac{\lambda}{2\pi R_0} \right)^3 (\mu - 1)$$

According to the classical theory of radiation $\frac{4\pi e^2}{3mc^2}$ is the natural width of spectral lines, say $\Delta_0\lambda$. We have thus

$$(11') \quad \Delta\lambda = \Delta_0\lambda \left(\frac{\lambda}{2\pi R_0} \right)^3 (\mu - 1)$$

The same result can be obtained in quantum mechanics. For the sake of simplicity we consider again virtual oscillators of only one type. Their variable electric moment, induced by the electric field of the excited atom is (v.e.g. Born-Jordan, *Elementare Quantenmechanik*, p. 246, 17-19)

$$P^{(j)} = \frac{\mu - 1}{2\pi N} |\vec{E}|$$

or, since

$$|\vec{E}| = \frac{P^{(1)}}{r_{1j}^3} \sqrt{3 \cos^2 \theta_{1j} + 1},$$

$$P^{(j)} = \frac{\mu - 1}{2\pi N} \cdot \frac{P^{(1)}}{r_{1j}^3} \sqrt{3 \cos^2 \theta_{1j} + 1}$$

Putting this expression into

$$E_{1j} = \frac{1}{r_{1j}^3} P^{(1)} P^{(j)} \sqrt{3 \cos^2 \theta_{1j} + 1}$$

E_{1j} , being the energy of interaction of the two oscillators considered, we obtain

$$E_{1j} = \frac{\mu - 1}{2\pi N} \cdot \frac{P^{(1)2}}{r_{1j}^6} (3 \cos^2 \theta_{1j} + 1)$$

and, dividing by \hbar ($2\pi\hbar$ Planck's constant), the corresponding frequency displacement

$$\Delta\omega = \frac{P^{(1)2}}{\hbar} \cdot \frac{\mu - 1}{2\pi N} \cdot \frac{1}{r_{1j}^6} (3 \cos^2 \theta_{1j} + 1)$$

Integration of this expression yields (10), if we assume

$$P^{(1)} = e \sqrt{\frac{\hbar}{2\omega m}}$$

We notice that this is the absolute value of the element $P_{01}^{(1)}$ of the matrix that describes the electric moment of the linear oscillator. [v. l. c., p. 127, (27)c.]

A straightforward test of (10) or (11) is not possible at present, since R_0 has not been evaluated theoretically. Holtsmark³ assumes in the analogous case in his theory of resonance broadening that R_0 is the gas-kinetic collision radius, but then too great values for the line width are obtained.⁷ This assumption is also hardly compatible with condition (2). We shall, therefore, rather investigate whether reasonable values for R_0 are obtained from the observed shift. We calculate R_0 from (11)

$$(12) \quad R_0 = \lambda \sqrt[3]{\frac{1}{6\pi^2} \cdot \frac{e^2}{mc^2} \cdot (\mu - 1) \frac{1}{\Delta\lambda}}$$

or, introducing the numerical values for e , m , c

$$(12') \quad R_0 = \lambda \times 1.679 \cdot 10^{-5} \sqrt[3]{\frac{\mu - 1}{\Delta\lambda}}$$

Margenau obtained his mean distance of approach, R_1 , from a formula [v. l. c.,¹ (25)] similar to our formula (11). His numerical values for R_1 , calculated from the pressure shift of the absorption line Hg 2537, are given in the following table, together with R_0 , obtained from (12')

Perturbing gas	$\Delta\lambda$ for 1 atm.	R_0	R_1	$(\mu - 1) \cdot 10^4$
A	.0088	6.43A	4.8A	3.022
O ₂	.0079	6.67	5.0	3.031
CO ₂	.0078	7.85	6.2	4.895
H ₂	.0042	6.52	4.9	1.547

Since $R_0 \sim 1.3 R_1$, the frequency displacement (10) is, for the same values of the mean distance of approach, more than twice as great as that obtained from Margenau's formula. This result indicates that the influence of the dispersion forces upon the shift of spectral lines may be of greater importance than has been assumed hitherto.

Comparing (10), further, with the shift due to dielectric polarisation of the foreign gas,⁸

$$(13) \quad \Delta\omega \cong -9 \frac{\epsilon - 1}{4\pi} \cdot \frac{e^2}{h} N^{\frac{1}{2}}$$

where ϵ is the dielectric constant and $\epsilon - 1 \sim 2(\mu - 1)$, we find that the displacements (10) and (13) are, for pressures up to a few atmospheres, of the same order of magnitude, when $R_0 \sim 6.9 \cdot 10^{-8}$ cm. Since these values are rather large for the mean distance of approach, it is probable that except for very high pressures or great radii of the excited atoms, as for instance in the case of the higher series members of the alkali spectra,^{8,9} the red shift is mainly due to dispersion forces.

For the numerical values of R_0 calculated above, condition (4), viz., $b_1 \ll \omega_1^2$, is fulfilled, but there may be some doubts concerning the validity of condition (2). If the omission of higher order terms in $1/r$ in (3) were not justified, the displacement calculated from (10) might be too small. The values found for R_0 are, on the contrary, comparatively large. This indicates that it will be perhaps necessary to explain why the observed red shift is not greater, all the more since the displacement due to other perturbations, which also produce usually red shift, is certainly not negligible and has to be added to the coupling displacement. Perhaps this difficulty will disappear if the consideration of the coupling forces $a\dot{q}$ and $k\dot{q}$ can be justified.

II.

Coupling forces of the type $k\dot{q}$ would be of essential importance for the intensity distribution. It seems to be necessary to consider them, for if $k_1 = 0$, the additional transition probability (5) vanishes, and then no transfer of energy to the foreign gas molecules and no forced vibrations of these are possible.

From equations (1) the intensity distribution in absorption lines, which have been chiefly considered hitherto, is easily obtained, provided that the conditions (4) are valid and that all the coupling coefficients are constant. For simplicity we consider only one excited and one perturbing atom. The equations (1) run in this case

$$(14) \quad \ddot{q}_1 + 2x_1\dot{q}_1 + \omega_1^2 q_1 + a\ddot{q}_2 + 2k\dot{q}_2 + bq_2 = F(t) \\ a\ddot{q}_1 + 2k\dot{q}_1 + bq_1 + \ddot{q}_2 + 2x_1\dot{q}_2 + \omega_2^2 q_2 = F(t)$$

If the external force $F(t)$ can be represented by a Fourier integral

$$(15) \quad F(t) = \int_{-\infty}^{+\infty} F(\omega) e^{i\omega t} d\omega$$

an approximate solution is readily obtained Assuming

$$q(t) = \int_{-\infty}^{+\infty} q(\omega) e^{i\omega t} d\omega$$

and comparing both sides of (13), we get

$$(-\omega^2 + 2x_1 i\omega + \omega_1^2) q_1(\omega) + (-\omega^2 a + 2ki\omega + b) q_2(\omega) = F(\omega)$$

$$(-a\omega^2 + 2ki\omega + b) q_1(\omega) + (-\omega^2 + 2x_2 i\omega + \omega_2^2) q_2(\omega) = F(\omega)$$

and hence

$$(16) \quad q_1(\omega) = \frac{F(\omega) [1 - H(g + 2ik\omega)]}{-\omega^2 + \omega_1^2 - H(g^2 - k^2\omega^2) + 2i\omega(x_1 - 2Hkg)}$$

$$q_2(\omega) = \frac{F(\omega) H[-\omega^2 + \omega_1^2 + 2ix_1\omega - (g + 2ik\omega)]}{-\omega^2 + \omega_1^2 - H(g^2 - k^2\omega^2) + 2i\omega(x_1 - 2Hkg)}$$

where

$$(17) \quad \omega_2^2 + 2x_2 i\omega - \omega^2 = 1/H, \quad -a\omega^2 + b = g$$

An approximate expression for the intensity distribution is obtained by calculating the average value of $F(\omega) e^{i\omega t} \frac{d}{dt} [q(\omega) e^{i\omega t}]$, to which only the imaginary part of $q(\omega)$ yields a non-vanishing contribution. Since perceptible absorption occurs only in a narrow frequency interval, we may put $F(\omega_1) = F(\omega)$ and $\frac{\omega}{\omega_1} = 1$. If we suppose, further, $F(\omega_2) = 0$, we may omit x_2 . Putting

$$(18) \quad \omega_1' = \omega_1 - \frac{1}{2\omega_1} H(g^2 - k^2\omega^2)$$

and

$$(18') \quad x' = x_1 - 2Hkg$$

we obtain

$$(19) \quad J(\omega) = \text{Const.} \frac{x' [1 + H(\omega_1^2 - \omega^2 - 2g)] + (\omega_1' - \omega) 2H(2k - x_1)}{(\omega_1' - \omega)^2 + x'^2}$$

Terms of order higher than the second in the coupling coefficients can be omitted, if conditions (4) hold. For the same reason ω can be replaced in H , ω_1' , and x' by ω_1 , since, over the frequency interval considered, $|\omega - \omega_1|$ or $|\omega - \omega_1'| \sim H/2\omega |g^2 - k^2\omega^2|$ or $|x_1 - 2Hkg|$. (19) is then reduced to

$$(20) \quad J(\omega) = \text{Const.} \frac{x'}{(\omega_1' - \omega)^2 + x'^2}$$

If equations (1) are solved for any number of perturbers, the same formula (20) is obtained with

$$(21) \quad \omega_1' = \omega_1 - \frac{H}{2\omega_1} \sum_{i=2}^n [(a_{1i}\omega_1^2 - b_{1i})^2 - k_{1i}^2\omega_1^2]$$

$$x' = x_1 - 2H \sum_{i=2}^n k_{1i} (a_{1i}\omega_1^2 - b_{1i})$$

in full agreement with (5) and (6). The assumption of coupling forces of the above type thus yields the same intensity distribution as the theory of impact broadening, and at the same time a shift of the whole line, or statistically, both shift and asymmetric broadening. But this result is, so far as the coupling forces are concerned, of a merely heuristic value.

The following possibilities would require further investigation. The quantum mechanical exchange forces can be described by equations of a form similar to

$$(23) \quad \begin{aligned} \dot{q}_1 - (i\omega_1 - x_1) q_1 + a\dot{q}_2 - ib'q_2 &= F'(t) \\ a\dot{q}_1 - ib'q_1 + \dot{q}_2 - i\omega_2'q_2 &= F'(t) \end{aligned}$$

where

$$(24) \quad \omega_2' = (\omega_1^2 + \omega_2^2) \frac{1}{2\omega_1}, \quad b' = \frac{1}{2} \left(a\omega_1 + \frac{b}{\omega_1} \right) + ik, \quad F' = \frac{F}{2\omega_1}$$

The equations (23) lead to the same results as the second order equations (13). It is thus possible that the influence of the assumed coupling forces $k\dot{q}$ and $a\dot{q}$ indicates a similar influence of the exchange forces.

Suppose the observed line width is partially due to the coupling forces $k\dot{q}$. In this case, since the shift is of the same order of magnitude as the line width

$$| (a\omega^2 - b)^2 - k^2\omega^2 | \sim | k\omega (a\omega^2 - b) |$$

hence also

$$(25) \quad | k\omega | \sim | a\omega^2 - b |$$

If, further, $a\omega^2$ and b were of the same order of magnitude, their difference might be comparatively small. In this case the violet shift, $+\frac{1}{2}Hk^2\omega$, could be greater than the red shift, $-\frac{1}{2\omega_1}H(a\omega_1^2 - b)^2$. This consideration suggests that perhaps the exchange forces, which are most important for hydrogen and helium, might be responsible for the violet shift, produced frequently by these gases. Heavy gases, on the contrary, for which, certainly, the ordinary electrostatic forces are of decisive importance, always produce red shift.

Classical principles suggest another possibility. Suppose $\sum_{i,j}^n a_{ij} \dot{q}_i \dot{q}_j$ can

be considered as part of the kinetic energy of the coupled system. For variable coupling coefficients a_{ij} we obtain then

$$(26) \quad k_{ij} = a_{ij} \sim \nabla a_{ij} \cdot v$$

where v is the relative velocity of the atoms or molecules considered. Since k is proportional to v , the violet shift, $\frac{1}{2} h k^2 \omega$, would be greater for light than for heavy gases, as is actually the case.

If, as this consideration suggests, the changes of the coupling coefficients were of essential importance, our previous assumption that they are approximately constant, is no longer justified. The general case of equations with variable coefficients will be considered in the next section

III.

The differential equations of vibrating systems with not too rapidly variable coefficients can be solved by successive approximation. Before resuming our former problem we consider the equation

$$(27) \quad \ddot{q} + 2 [x + x'(t)] \dot{q} + \omega_0^2 \left(1 + \frac{\epsilon(t)}{\omega_0} \right) q = F(t)$$

where $\omega_0 \sqrt{1 + \epsilon(t)/\omega_0}$ is the variable frequency and $x'(t)$ the additional transition probability, which may assume both positive and negative values. If we put

$$q = q_0 + q_1'$$

where q_0 is the solution of the unperturbed equation, we obtain

$$\dot{q}_1' + 2 [x + x'(t)] \dot{q}_1' + \omega_0 [\omega_0 + \epsilon(t)] q_1' = - 2x'(t) \dot{q}_0 - \omega_0 \epsilon(t) q_0$$

Similarly

$$q_n' = q_n + q_{n+1}'$$

q_n being a solution of

$$\ddot{q}_n + 2x\dot{q}_n + \omega_0^2 q_n = - 2x'(t) \dot{q}_{n-1} - \omega_0 \epsilon(t) q_{n-1}$$

and

$$(28) \quad q(t) = \sum_{i=0}^{\infty} q_i(t)$$

provided that this series is convergent. The equation for $q_n(t)$ can be solved with the help of Fourier's integral theorem. Suppose $q_{n-1}(t)$ is known, then

$$(29) \quad q_n(\omega) = \frac{1/2\pi}{\omega^2 - 2ix\omega - \omega_0^2} \int_{-\infty}^{+\infty} [2x'(t) \dot{q}_{n-1}(t) + \omega_0 \epsilon(t) q_{n-1}(t)] e^{-i\omega t} dt$$

and

$$(30) \quad q_n(t) = \int_{-\infty}^{+\infty} q_n(\omega) e^{i\omega t} d\omega$$

The negative imaginary part of

$$q(\omega) = \sum_{i=0}^{\infty} q_i(\omega)$$

yields the intensity distribution (v 19).

If we want to obtain concrete results, we have to use appropriate functions for $x'(t)$ and $\epsilon(t)$. The most easily integrable function of the type required to describe variations of the frequency and transition probability during collisions is $P(t) e^{-t^2/\tau^2}$, $P(t)$ being a polynomial. τ is of the order of magnitude of the time during which the coupling interaction is strong. We assume for instance

$$(31) \quad x'(t) = \sum_i \left[x_{0i} + x_{1i} \frac{t - t_i}{\tau_i} + x_{2i} \frac{(t - t_i)^2}{\tau_i^2} \right] e^{-(t-t_i)^2/\tau_i^2}$$

$$(32) \quad \epsilon(t) = \sum_i \left[\epsilon_{0i} + \epsilon_{1i} \frac{t - t_i}{\tau_i} + \epsilon_{2i} \frac{(t - t_i)^2}{\tau_i^2} \right] e^{-(t-t_i)^2/\tau_i^2}$$

t_i being the moment of strongest interaction for the i -th collision. An expression for $q_1(\omega)$ is readily obtained. With the same assumptions as above (15 f. f.) we have

$$q_0(\omega) = F(\omega_0) \frac{1}{\omega_0^2 + 2ix\omega - \omega^2}$$

Integrating by complex variables we get (v 30)

$$(33) \quad q_0(t) = -\frac{2\pi}{\omega_1} \cdot iF(\omega_0) e^{(i\omega - x)t}$$

and with this function from (29)

$$q_1(\omega) = F(\omega_0) \int_{-\infty}^{+\infty} \frac{1}{\omega^2 - \omega_0^2 - 2ix\omega} \left[(x_0 - i\epsilon_0) + (x_1 - i\epsilon_1) \frac{t}{\tau} + (x_2 - i\epsilon_2) \frac{t^2}{\tau^2} \right] \times e^{-i(\omega_0 - \omega)t - x t - t^2/\tau^2} dt$$

if for simplicity only one collision is considered, for which $t_i = 0$. Integrating we obtain

$$(34) \quad q_1(\omega) = F(\omega_0) \cdot \frac{\tau\sqrt{\pi}}{2} \left\{ 2 \frac{(x_0 + x_2/4) - i(\epsilon_0 + \epsilon_2/4)}{\omega - \omega_0 - ix} - i\tau(x_1 - i\epsilon_1) - \frac{1}{2} \tau^2 (\omega - \omega_0 - ix)(x_2 - i\epsilon_2) \right\} \times \exp \left[-\frac{\tau^2}{4} (\omega - \omega_0)^2 + i \frac{\tau^2 x}{2} (\omega - \omega_0) \right]$$

We consider at first the dependence of the intensity distribution upon x_1 and ϵ_1 ,

$$(35) \quad J_1(\omega) = \text{Const.} \times \tau \left[x_1 \cos(\omega - \omega_0) \frac{\tau^2 x}{2} + \epsilon_1 \sin(\omega - \omega_0) \frac{\tau^2 x}{2} \right] \times e^{-\frac{\tau^2}{4} (\omega - \omega_0)^2}$$

Negative and positive values of the frequency displacement

$$\Delta\omega \cong \frac{1}{2} t \epsilon_1 e^{-t^2/\tau^2}$$

are in this case equally probable and the statistical distribution of the frequencies is symmetric. Nevertheless the actual intensity distribution is asymmetric, as is evident from the term containing ϵ_1 in (35). The statement that the method, based upon the Fourier analysis of the frequency variation,¹⁰ 'is inadequate for handling shifts and asymmetries...',² is thus not necessarily true. This possibility ought to be considered in some cases, for instance, when observed asymmetries, other causes being excluded, are attributed to an unresolved hyperfine structure¹¹

The formula for the intensity distribution derived from (34), is simplified, if x represents only the radiation damping, $x \sim 10^8 \text{ sec.}^{-1}$. If τ is probably of the order of magnitude of the time during which the distance of two colliding atoms is smaller than $\sim 10^{-7} \text{ cm}$. Thus $\tau \sim 10^{-11} - 10^{-13} \text{ sec}$, and $\tau x \ll 1$. From the exponential term in (34) it is further evident that absorption is perceptible only in a frequency interval where $|\omega - \omega_0| \tau \sim 1$, and therefore also $\left| (\omega - \omega_0) \frac{\tau^2}{2} \right| \ll 1$. The cosine of this expression can thus be replaced by 1, and the sine omitted. We obtain in this case the intensity distribution

$$(36) \quad J(\omega) = \text{Const.} \left\{ \frac{x}{(\omega - \omega_0)^2 + x^2} + \right. \\ \left. \tau \sqrt{\pi} \times \left[2 - \frac{x(x_0 + x_2/4)}{(\omega - \omega_0)^2 + x^2} + \frac{(\omega - \omega_0)(\epsilon_0 + \epsilon_2/4)}{(\omega - \omega_0)^2 + x^2} \right. \right. \\ \left. \left. + \tau x_1 + \frac{1}{2} \tau^2 \{(\omega - \omega_0) \epsilon_2 - x x_2\} \right] \times e^{-\frac{\tau^2}{4} (\omega - \omega_0)^2} \right\}$$

In the general case of many collisions we obtain instead of (34) a sum over expressions of the same type with $\left(\frac{\tau_i^2 x_i}{2} - t_i \right)$ instead of $\frac{\tau^2 x}{2}$. If we assume for simplicity $\tau_i = \tau$, $x_{0i} = x$, etc., we have to consider the sums

$$(37) \quad \sum_i \cos(\omega - \omega_0) \left[\frac{\tau_i^2 x_i}{2} - t_i \right] = \sum_i \cos(\omega - \omega_0) t_i$$

$$(37') \quad \sum_i \sin(\omega - \omega_0) \left[\frac{\tau_i^2 x_i}{2} - t_i \right] = \sum_i \sin(\omega - \omega_0) t_i$$

The terms containing $\sin(\omega - \omega_0) \frac{\tau^2 x}{2}$ are omitted as above and $\cos(\omega - \omega_0) \times \frac{\tau^2 x}{2}$ is replaced by 1. The sum over the sines becomes very small, when many collisions are taken into account, since both negative and positive values of the terms are equally probable. We may expect that the

calculation of (37) by means of statistical methods will lead to a function of ω , containing as a parameter the mean time between two successive collisions, say T , and decreasing for $|\omega - \omega_0| > \frac{2\pi}{T}$. Denoting this function by $f(\omega, T)$, we shall have (v. 36)

$$(38) \quad J(\omega) = \text{Const} \times \left[(\omega - \omega_0)^2 + x^2 + f(\omega, T) \tau \sqrt{\pi} \{c. (36)\} e^{-\frac{\tau^2}{4}(\omega - \omega_0)^2} \right]$$

The function $f(\omega, T)$ represents the ordinary impact broadening, but with our assumptions there is no indication that $\frac{1}{T}$ could be simply added to x as in Lorentz' theory of impact broadening where it determines the line width directly. Our results show that not only T , as has been assumed hitherto, but also τ and the type of the collision process are of considerable, if not decisive, importance for the intensity distribution

Equations (13) with variable coefficients can be solved in a similar way. We assume

$$(39) \quad \begin{aligned} a(t) &= (a_0 + a_1 t/\tau) e^{-t^2/\tau^2} \\ b(t) &= (b_0 + b_1 t/\tau) e^{-t^2/\tau^2} \\ k(t) &= (k_0 + k_1 t/\tau) e^{-t^2/\tau^2} \end{aligned}$$

From the solution for uncoupled vibrators

$$q_{10} = e^{i\omega_1^* t}, \quad q_{20} = 0$$

where for simplicity the amplitude constant has been omitted and $\omega^* = \omega + ix$ we obtain as before (v. 29)

$$q_{21}(\omega) = \frac{\frac{1}{2}\pi}{\omega_2^2 - \omega^2} \int_{-\infty}^{+\infty} [a(t) \ddot{q}_{10} + k(t) \dot{q}_{10} + b(t) q_{10}] e^{-i\omega t} dt$$

and integrating

$$q_{21}(\omega) = \frac{\tau H}{\sqrt{\pi}} [A_0 + \frac{1}{2} i\tau (\omega_1^* - \omega) A_1] \times e^{-\frac{\tau^2}{4}(\omega_1^* - \omega)^2}$$

where

$$\begin{aligned} A_0 &= a_0 \omega_1^{*2} - i k_0 \omega_1^* - b_0 \\ A_1 &= a_1 \omega_1^{*2} - i k_1 \omega_1^* - b_1 \end{aligned}$$

and within the narrow frequency interval considered

$$H = \frac{1}{\omega_2^2 - \omega^2} \cong \frac{1}{\omega_2^2 - \omega_1^2}$$

We obtain further (v. 30)

$$\begin{aligned} (40) \quad q_{21}(t) &= \int_{-\infty}^{+\infty} q_{21}(\omega) e^{i\omega t} d\omega \\ &= 4H (A_0 + A_1 t/\tau) e^{-\frac{t^2}{\tau^2}} q_{10}(t) \end{aligned}$$

If $\frac{1}{\tau} \ll \omega$, we obtain a sufficient approximation, putting

$$\dot{q}_{21} = i\omega^* q_{21}(t), \quad \ddot{q}_{21} = -\omega_1^{*2} q_{21}(t)$$

in the first of equations (13), which becomes

$$(41) \quad \ddot{q}_1 + \kappa \dot{q}_1 + [\omega_1^2 + \epsilon(t) \omega_1] q_1 = F(t)$$

with

$$(42) \quad \epsilon(t) = -4H/\omega_1 \times (A_0 + A_1 t/\tau)^2 e^{-t^2/\tau^2}$$

If we wish to consider only the asymmetries, we can omit the imaginary part of $\epsilon(t)$, which describes the variation of the transition probability and indicates symmetric broadening. Comparing the real part of (42) and (32), we see that

$$(43) \quad \begin{cases} \epsilon_0 = \frac{4H}{\omega_1} [(a_0 \omega_1^2 - b_0) - k_0^2 \omega_1^2] \\ \epsilon_1 = 0 \\ \epsilon_2 = \frac{4H}{\omega_1} [(a_0 \omega_1^2 - b_0) - k_0^2 \omega_1^2] \end{cases}$$

We obtain thus for the asymmetric part of the intensity distribution (v 36,38)

$$(44) \quad J_a(\omega) = \text{Const} \times f(\omega, T) \times \left\{ \frac{2(\omega_1 - \omega) [(a_0 \omega_1^2 - b_0)^2 - k_0^2 \omega_1^2]}{(\omega_1^2 - \omega)^2 + \kappa^2} \right. \\ \left. + \frac{1}{2} \tau^2 (\omega_1 - \omega) [(a_1 \omega_1^2 - b_1)^2 - k_1^2 \omega_1^2] \right\} e^{-\frac{\tau^2}{4} (\omega - \omega_2)^2}$$

It is evident from this formula that the asymmetric broadening and the shift of spectral lines agree as to their sign with the frequency displacement (6), which has been calculated for constant coupling forces. It seems, however, that the form of spectral lines is chiefly determined by the way in which the coupling forces vary with time. We see that the influence of the assumed coupling forces, as expressed by the functions $a_0 e^{-t^2/\tau^2}$, and $a_1 t/\tau \times e^{-t^2/\tau^2}$, is quite different. The former determine the intensity distribution chiefly in the central parts of the spectral line and the latter in the wings. These results indicate that it may be possible to derive some conclusions concerning the nature of the interaction forces from the form of spectral lines.

The assumed generalisation of coupling forces leads, as we have seen, to results which are in qualitative agreement with experiment. But we have still to investigate, whether formulæ, analogous to that obtained for the red shift (11), can be also obtained for the width and the violet shift of spectral lines; and, further, we have to represent the interactions by the proper functions of time, so that the formulæ for the intensity distribution could be tested experimentally.

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ULTRASONIC VELOCITIES IN SOME ORGANIC LIQUIDS—PART II.

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1. Introduction.

IN a paper appearing in the *Proceedings of the Indian Academy of Sciences*, Vol. II, p. 497 (1935), the author gave determinations of ultrasonic velocities in 52 organic liquids. It was thought that it would be of interest to find out the velocities in some related groups of organic liquids. In the present paper, results of both ultrasonic velocities and adiabatic compressibilities are given for di-esters, for the xylenes and for two bases, quinoline and *o*-toluidine.

The complete experimental arrangement has been described in the earlier paper *

In these experiments, the liquids which were distilled, were contained in a cubic glass cell of 100 c.c. capacity, bigger than the vessel used previously. They were all of the purest stock, from Kahlbaum or Merck or Dr. Schukardt or de Haen.

The frequency employed for the vibration was 7.37×10^6 cycles per second. The temperatures at which the determinations were made, are noted against each liquid.

2. Results.

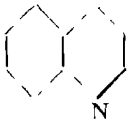
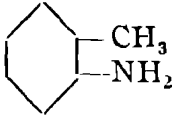
The following table contains the results of determinations of ultrasonic velocities in 14 organic liquids. The last column gives the calculated adiabatic compressibilities from the known acoustic velocities.

* In a private communication to the author, Professor J. C. Hubbard has explained the two points raised in the earlier paper on page 504.

TABLE I. *Ultrasonic velocities at 7.37×10^6 cycles/second.*

Liquids	Chemical Formula	Temp in °C	Wave- length of sound in mms	Velo- city of sound in meters per second	Adiaba- tic com- pressibi- lity $\beta \times 10^6$
<i>o</i> -Xylene	$C_6H_4 (CH_3)_2$	22°	0.1831	1352	62.4
<i>m</i> -Xylene	„ „	22°	0.1800	1328	65.9
<i>p</i> -Xylene	„ „	22°	0.1805	1330	65.9
Diethyl oxalic ester	$\begin{array}{c} COO \cdot C_2H_5 \\ \\ COO \cdot C_2H_5 \end{array}$	22°	0.1888	1392	48.0
Diethyl malonic ester	$\begin{array}{c} COO \cdot C_2H_5 \\ CH_2 \\ COO \cdot C_2H_5 \end{array}$	22°	0.1879	1386	49.6
Diethyl succinic ester	$\begin{array}{c} CH_2 \cdot COOC_2H_5 \\ \\ CH_2 \cdot COOC_2H_5 \end{array}$	22°	0.1869	1378	50.7
Diethyl adipic ester	$\begin{array}{c} CH_2 \cdot CH_2 \cdot COOC_2H_5 \\ \\ CH_2 \cdot CH_2 \cdot COOC_2H_5 \end{array}$	22°	0.1866	1376	52.7
Diglycollic ester	$\begin{array}{c} CH_2 \cdot COOC_2H_5 \\ O \\ CH_2 \cdot COOC_2H_5 \end{array}$	22°	0.1947	1435	43.9
Thiodiglycollic ester	$\begin{array}{c} CH_2 \cdot COOC_2H_5 \\ S \\ CH_2 \cdot COOC_2H_5 \end{array}$	22° .5	0.1966	1449	41.7
Methyl adipate	$\begin{array}{c} CH_2 \cdot CH_2 \cdot COO \cdot CH_3 \\ \\ CH_2 \cdot CH_2 \cdot COO \cdot CH_3 \end{array}$	21° .8	0.1994	1469	43.9

TABLE I—(contd.)

Liquids	Chemical Formula	Temp in °C.	Wave- length of sound in mms	Velo- city of sound in meters per second	Adiaba- tic com- pressibi- lity $\beta\phi \times 10^6$
Acetone dicarboxy- lic ester	$\begin{array}{c} \text{CH}_2 \cdot \text{COO} \cdot \text{C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{CO} \\ \diagdown \quad \diagup \\ \text{CH}_2 \text{ COO} \cdot \text{C}_2\text{H}_5 \end{array}$	22°·5	0·1828	1348	50·7
Quinoline		22°	0·2228	1643	34·0
<i>o</i> -Toluidine		22°·5	0·2265	1669	36·1
Methyl hexaline	$\text{C}_6\text{H}_{10}(\text{CH}_3) (\text{OH})$	22°	0·1936	1428	53·7

Of the liquids studied here, data of previous determinations are available only for four liquids. We give below, in Table II, values for comparison with those obtained earlier.

 TABLE II.
 Velocities in meters/second.

Liquids	Audio range from I C T	R Bar. Freq about $7 \cdot 5 \times 10^6$ c/s	Author Freq $7 \cdot 37 \times 10^6$ c./s.
<i>o</i> -Xylene	—	1345 at 21° C	1352 at 22° C.
<i>m</i> -Xylene	—	1330 at 21° C.	1328 „ „
<i>p</i> -Xylene	—	1333	1330 „ „
<i>o</i> -Toluidine	1645 at 21° C.	—	1669 „ 22°·5 C.
<i>m</i> -Toluidine	1602·4 at 21°·6 C.	—	—

R. Bär's results are taken from a paper by him appearing in *Helv. Phys. Acta* 1933, 6, 578, while for the audio range, the value for *o*-toluidine is taken from the *International Critical Tables*. The velocity for *m*-xylene has already been given in the earlier paper. The results are in good agreement.

3. Discussion.

Remarks of a general kind were made in the earlier paper, of the relation between sound velocities and chemical constitution. We shall, however, go more elaborately in this paper.

The xylenes: The sound velocity in the ortho-compound is higher than in the other two xylenes which have approximately the same velocities. Substitution in the ortho position favours greater sound velocity. Even for the toluidines, ortho has the higher velocity (see Table II)

The di-esters (ethyl): In the series, oxalic, malonic, succinic and adipic esters, the sound velocity decreases with increasing weights of the radical. The same effect was noticed in the earlier paper, on the ethyl esters of formic, acetic, propionic and butyric acids. In the latter group, ethyl formate has a velocity of 1263 m./s, those for the remaining compounds being 1187, 1185 and 1171 m./s respectively. This is quite the reverse of what obtains in hydrocarbons and alcohols, the sound velocity increasing with the length of the chain.

Ethyl and methyl adipates: Introduction of a methyl radical instead of an ethyl radical in an ester, enhances the sound velocity. That this is true can be seen from the earlier results also, given below:

Liquids	Velocity of sound in meters/second
Ethyl adipate	1376
Methyl „	1469
Ethyl acetate	1187
Methyl „	1211
Ethyl propionate	1185
Methyl „	1215

In all the cases above given, even though the length of the chain increases, by the introduction of an ethyl in place of a methyl radical, there is a decided diminution in velocity. Variations in density alone cannot account for this anomaly.

Thio- and di-glycollic esters : In the thio-compound an atom of sulphur replaces an atom of oxygen in the diglycollic ester. The velocity is enhanced in the thioglycollic ester. But it was observed in the earlier paper that the introduction of a heavy atom usually lowered the sound velocity ; *cf.* carbon tetrachloride and chloroform ; methylene chloride and methylene bromide. When we find that the esters behave differently from alcohols or hydrocarbons in the matter of velocity of sound, and when we know that we are now dealing with these two esters, it is not difficult to understand why it should be so.

o-toluidine and quinoline : The ultrasonic velocity in *o*-toluidine is much higher than that for toluene, but nearer to that of aniline ; to which it is related, being less by about 15 meters. Quinoline, another base, has a velocity higher than that for either pyridine or benzene. Bases usually show higher sound velocities than the corresponding hydrocarbons.

The author thanks Sir C. V. Raman, Kt., for his interest in the work.

Summary.

The paper contains determinations of ultrasonic velocities in 14 organic liquids, some of them being di-esters, by the method of diffraction of light by high frequency sound waves. Included are also adiabatic compressibilities for these compounds, calculated therefrom.

PHYSICAL PRINCIPLES AND APPLICATIONS OF MAGNETO-CHEMISTRY

by Prof. S. S. Bhatnagar and Dr. K. N. Mathur.

By C. V. RAMAN.

It has long been familiar to chemists that optical properties such as refraction, dispersion and optical activity furnish very useful indications of molecular constitution. The importance of the study of dielectric behaviour and the significance of the electric moment of the molecule has also of late been appreciated by workers in the field of chemistry. The fundamental importance of studies of magnetic behaviour from a chemical point of view has not, however, received the same degree of general recognition, and this may in part be due to the lack of suitable texts dealing specially with magneto-chemistry. Van Vleck's "Electric and Magnetic Susceptibilities" (1932) in which the theoretical aspects of magnetism are handled in a masterly manner is accessible only to one fairly well equipped with mathematical knowledge. F. C. Stoner's "Magnetism and Matter" (1934) is less severely mathematical and devotes more space to the experimental aspects of the subject and is consequently within the reach of a wider circle of readers. There remained nevertheless a distinct need for a book addressed primarily to the chemist and dealing with magnetism from the chemical standpoint; and it may be said at once that this gap has been satisfactorily filled by the book now under review.

The book has several pleasing features. It covers the field in an adequate manner and presents the subject in the proper historical perspective. It includes an account of experimental methods which should be useful to the intending researcher, and sufficient theory to form at least a beginning to a deeper knowledge of the subject. There are useful tables of data and adequate references to the literature. The treatment endeavours to be critical without being unduly severe on opinions or statements with which the authors disagree. The classical investigations, and the latest researches alike receive their due share of attention. It is specially pleasing to notice the numerous references to work done at various centres of research in India in the subject, but the space given to such references does not appear to be greater than the intrinsic importance of the contributions referred to demands. Taken altogether, the book is a production which does great credit to the

authors and will, it is hoped, be widely used. It is easy to see that the authors are thoroughly familiar with their subject, as might well be expected from the fact that their own original contributions are significant in volume and quality. It is some satisfaction to find that the leading Indian investigators, such as the writers of this book, are entering the field of authorship as producers of advanced scientific treatises. It is difficult and laborious work but is very necessary for gaining recognition for themselves and for Indian centres of learning as sources of new knowledge.

A perusal of the book indicates that there is yet an immense field of research awaiting the explorer in magneto-chemistry. There is much to be done before the mass of empirical experience in the magnetic behaviour of the ferrous metals and their alloys is reduced to a coherent body of knowledge. In the study of para- and dia-magnetic susceptibilities and their variations with physical condition and chemical constitution, there is an almost illimitable territory of research. The study and interpretation of magne-crystallic action, both of dia- and of para-magnetic compounds such as is being pursued with success by K. S. Krishnan and his collaborators at Calcutta, promises results of real importance. The remarkable differences in the magnetic character and anisotropy of the molecules of the aliphatic and aromatic compounds disclosed by recent investigations are obviously connected with the deepest problems of organic chemistry. It is greatly to be hoped that these will be further studied and elucidated.

GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part II* *Cis To Trans.*

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AND

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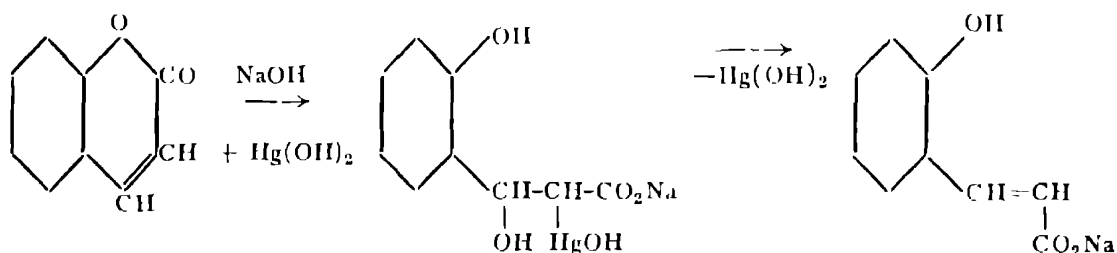
IN discussing the mechanism of geometrical inversion in the acids derived from the coumarins (Seshadri, 1934) it was pointed out that *cis* to *trans* inversion takes place in an alkaline medium in which coumarins first form alkali salts of coumarinic acids and that addition of some addenda at the double bond is a requisite preliminary to the final inversion to the coumaric acids. In that connection mention was made that the results of the action of mercury compounds on coumarins (Sen and Chakravarti, 1929 and 1930) could be explained as due to the influence of substituent groups present in the benzene or pyrone ring. With a group of coumarins as exemplified by 6-nitro- and 6 : 8-dibromocoumarins they obtained coumaric acids whereas with others which contained alkyl and hydroxyl groups they obtained mercurated compounds.

According to the above-mentioned mechanism coumarin itself should give rise to coumaric acid or mercurated coumaric acid. By the action of sodium hydroxide and mercuric acetate in the cold Sen and Chakravarti (*loc. cit.*) reported the isolation of a diacetoxymercuricoumaric acid whereas Naik and Patel (1934), using apparently the same method, claimed to have obtained 6 : 8-bisacetoxymercuricoumarin. By boiling, however, an alkaline solution of coumarin with mercuric oxide, the former authors stated, that they obtained mercurated coumarins. The reaction of alkali and mercuric acetate has now been investigated by us following Sen and Chakravarti's procedure and the product is found to be as they claimed a mercurated coumaric acid and not a mercurated coumarin (*cf.* Naik and Patel). By the mercuric oxide method of the same authors was obtained a compound which they believed to be 6-chloromercuricoumarin and which is now found to be also a mercurated coumaric acid. It dissolves in aqueous sodium carbonate and bicarbonate and yields coumaric acid readily when hydrogen

* Part I of this series was published in *J. I. C. S.*, 1934, 743-49.

sulphide is passed into an alkaline solution of the compound in order to precipitate the mercury and subsequently the filtered solution is acidified. In the presence of cold caustic alkali and yellow mercuric oxide coumarin undergoes transformation into coumaric acid so easily that this inversion could not have failed to take place under the conditions mentioned above. Based upon this observation a very rapid and cheap method has been worked out for the preparation of pure coumaric acid from coumarin. 7-methylcoumarin behaves similarly and gives rise to a good yield of 4-methylcoumaric acid whereas 6-nitrocoumarin is unaffected in the cold even after treatment for several hours. Only the unstable nitro-coumarinic acid is produced which rapidly reverts to the nitrocoumarin. But at the boiling point the inversion takes place fairly easily giving rise to a good yield of 5-nitrocoumaric acid. Under these vigorous conditions coumarin and methylcoumarin undergo mercuration besides inversion and so produce mercurated coumaric acids.

The part played by mercuric oxide in effecting the inversion may be represented as below



It adds on to the double bond in the *cis* stage and after the required rotation of the groups has taken place gets eliminated from the *trans* stage. In support of this may be mentioned (1) observations in which *cis* compounds add on mercury compounds readily whereas the corresponding *trans* compounds do not react or do so only slowly under the same conditions (Büilmann, 1912; Wright, 1935) and (2) the easy decomposition in the presence of alkali of addition compounds like methoxymellitic acid and sodium dihydrocoumaric acid- β -sulphonate to give coumaric acid. The greater difficulty with which *trans* inversion takes place with 6-nitrocoumarin by the present method agrees with previous experience using other methods (Dey and Row, 1924; Dey, Rao and Seshadri, 1934). This may be attributed to the nature of the nitrogroup as an electron sink which diminishes the tendency to undergo inversion.

Experimental

Preparation of *O*-coumaric acid.—Finely powdered coumarin (8 g.) was treated with cold aqueous caustic soda (8 g. in 100 c.c.), yellow mercuric

oxide (1 g) added and the mixture shaken vigorously for ten minutes. Coumarin dissolved rapidly and the solution assumed a light yellow colour with a green fluorescence. It was then filtered through an ordinary filter without suction, the residue washed twice with small quantities of water and the collected filtrate acidified with concentrated hydrochloric acid. The colourless crystalline precipitate that was obtained was filtered at the pump and washed with small quantities of water. The yield was almost theoretical and the acid was pure melting at 208–10° (decomp). When tested by passing hydrogen sulphide into an alkaline solution of the acid it gave no precipitate of mercuric sulphide thereby showing that it was free from mercury. Care should be taken that no rise of temperature takes place as otherwise some mercuration is effected.

4-Methylcoumaric acid was prepared from 7-Methylcoumarin (5 g) by closely following the above procedure. The yield of the pure acid melting at 195–6° was 5 grams.

5-Nitrocoumaric acid could not be obtained by treatment in the cold as above. Only the unstable coumarinic acid was formed which reverted rapidly into the original nitrocoumarin. It was therefore made by following the method of Sen and Chakravarti (1930). The following modification of their method was found to give better yields. After boiling 6-nitrocoumarin in alkaline solution with mercuric oxide the crude nitrocoumaric acid was precipitated with hydrochloric acid and then purified by treatment with sodium bicarbonate instead of ammonia and by subsequent precipitation of the pure acid. This minimised contamination with unchanged nitrocoumarin which dissolved to a considerable extent in ammonia and only sparingly in sodium bicarbonate. Yield of the pure acid after crystallisation from alcohol was 4.5 grams from 5 grams of the nitrocoumarin.

Action of sodium hydroxide and mercuric acetate on coumarin—By following the procedure of Sen and Chakravarti a compound (diacetoxymercurocoumaric acid) was obtained which exhibited all the properties and reactions mentioned by them. It dissolved easily in cold aqueous sodium carbonate and bicarbonate and was therefore a diacetoxymercurocoumaric acid and not a coumarin.

For obtaining pure coumaric acid from it the method of Sen and Chakravarti—boiling with dilute hydrochloric acid—was not found to be suitable. Removal of mercury was not always complete so that the product frequently melted low. A convenient method is to dissolve the mercurated compound in dilute ammonia and pass hydrogen sulphide till the precipitation of mercury sulphide is complete. It is then filtered and the clear filtrate acidified with

hydrochloric acid. The crystalline precipitate melts with decomposition at 208-210° when filtered and washed with water and is found to be pure coumaric acid.

Action of hot sodium hydroxide and mercuric oxide on coumarin—The product that was considered by Sen and Chakravarti to be 6-chloromercuri-coumarin was prepared by their method (1929, p 851). It was a colourless partly crystalline powder melting with decomposition at about 180° and was found to be soluble in aqueous sodium carbonate and sodium bicarbonate with evolution of carbon dioxide. Pure coumaric acid was obtained easily from it by the hydrogen sulphide method described above. It was therefore a mercurated coumaric acid and not a coumarin. It should be mentioned that these mercuration products underwent marked change when preserved over long periods and their solubility in aqueous sodium carbonate diminished.

Summary.

A rapid and efficient method has been found for preparing coumaric acid and 4-methylcoumaric acid from coumarin and 7-methylcoumarin respectively by treatment with mercuric oxide in the presence of cold alkali. 5-nitrocoumaric acid is not produced in the cold and is formed only by boiling the mixture of 6-nitrocoumarin, mercuric oxide and alkali. The action of cold alkali and mercuric acetate or of hot alkali and mercuric oxide on coumarin yields mercurated coumaric acids. From these pure coumaric acid can be produced by using ammonia and hydrogen sulphide.

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ULTRASONIC VELOCITIES IN LIQUID MIXTURES.

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1. Introduction.

IN an earlier paper¹ the author gave experimental determinations of ultrasonic velocities in a number of organic liquids by the method of diffraction of light by sound waves of high frequency. The present paper deals with ultrasonic velocities in mixtures of organic liquids by the same experimental method, as such information will be valuable for calculating the compressibilities of liquid mixtures.

The experimental arrangement is the one followed in earlier investigations, and it has been described in full.

All the usual precautions which may vitiate the results have been duly taken and since they have been fully discussed already, we shall not repeat them here.

The liquids used were of the purest stock, used after distillation. The densities of the pure liquids and of the mixtures were determined by a specific gravity bottle. For mixtures, as soon as the additional quantity of the second component was added to the first component contained in a stoppered conical flask, the mixture was thoroughly shaken, and the density determined in the usual way. The concentrations were found out from the weights of the second component added, from time to time.

All the experiments were carried out at 23° C. which was the temperature maintained in the room. The frequency employed was 7.37×10^6 cycles per second.

2. Results.

Four binary liquid mixtures of,

- (1) Benzene and carbon tetrachloride ;
- (2) Carbon disulphide and carbon tetrachloride ;
- (3) Ethyl acetate and carbon tetrachloride ; and
- (4) Tetralin and carbon tetrachloride

have been studied for ultrasonic velocities at various concentrations. Incidentally, the adiabatic compressibilities were also calculated for the mixtures.

¹ S. Parthasarathy, *Proc. Ind. Acad. Sci.*, 1935, 2, 497.

The results of investigations in these four liquid mixtures are given in four tables. Column five contains experimental results of ultrasonic velocities, column three the densities and column six the adiabatic compressibilities calculated therefrom.

TABLE I

(a) *Mixture of Benzene and Carbon Tetrachloride ; at 23°C.*

	Benzene % by weight	CCl ₄ % by weight	Density	Wave-length of sound in mms	Velocity of sound in meters/sec.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0.8725	0.1780	1312	66.4
2	72.1	27.9	1.001	0.1629	1201	69.2
3	56.6	43.4	1.086	0.1545	1139	71.0
4	35.2	64.8	1.237	0.1422	1048	73.5
5	23.0	77.0	1.340	0.1381	1018	72.0
6	..	100	1.596	0.1258	927.2	72.9

TABLE II.

(b) *Mixture of Carbon Disulphide and Carbon Tetrachloride ; at 23° C.*

	CS ₂ % by weight	CCl ₄ % by weight	Density	Wave-length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	1.258	0.1560	1150	60.1
2	73.1	26.9	1.331	0.1479	1090	63.3
3	58.1	41.9	1.374	0.1123	1049	66.2
4	39.2	60.8	1.436	0.1373	1012	68.1
5	20.0	80.0	1.502	0.1320	972.7	70.4
6	..	100	1.596	0.1258	927.2	72.9

TABLE III

(c) *Mixture of Ethyl Acetate and Carbon Tetrachloride ; at 23° C.*

	Ethyl acetate % by weight	CCl ₄ % by weight	Density	Wave-length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0.8989	0.1605	1184	79.3
2	69.6	30.4	1.034	0.1517	1119	77.3
3	40.9	59.1	1.200	0.1425	1051	75.5
4	25.1	74.9	1.313	0.1361	1003	75.7
5	16.4	83.6	1.404	0.1336	984.2	73.5
6	..	100	1.596	0.1258	927.2	72.9

TABLE IV.

(d) Mixture of Tetralin and Carbon Tetrachloride; at 23° C.

	Tetralin % by weight	CCl ₄ % by weight	Density	Wave length of sound in mms.	Velocity of sound in m./s.	Adiabatic compressibility $\beta\phi \times 10^6$
1	100	..	0.9681	0.1991	1468	18.0
2	67.3	32.7	1.125	0.1766	1301	52.5
3	45.6	54.4	1.240	0.1618	1192	56.7
4	28.8	71.2	1.348	0.1499	1105	60.8
5	18.1	81.9	1.424	0.1406	1036	65.1
6	..	100	1.596	0.1258	927.6	72.9

The three graphs, Fig. 1, Fig. 2 and Fig. 3, give the relation between (1) the concentration and the density, (2) the concentration and the ultrasonic

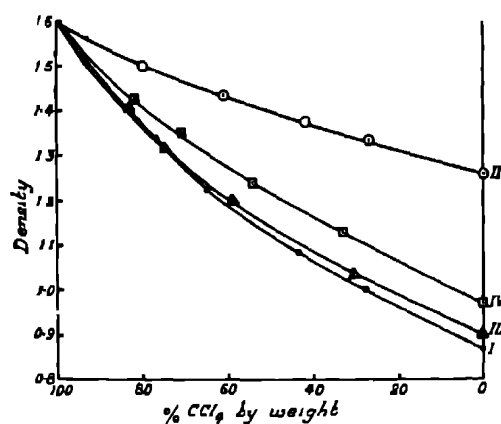


FIG 1.

velocity, and (3) the concentration and the adiabatic compressibilities of the mixtures. Along the concentration axis, only the weight percentage of carbon tetrachloride is mentioned, as this liquid is common to all, while the percentage of the second component can be easily obtained by simple difference. The curves are all numbered corresponding to the mixtures as given in the tables

3 Discussion

So far no direct determinations have been made of sound velocities in liquid mixtures. The method of diffraction of light by high frequency sound waves offers an easy and quick method for determining sound velocities and adiabatic compressibilities and this method has been applied to four liquid mixtures.

Fig. 2 shows that for mixtures (1) carbon tetrachloride and benzene, and (2) carbon disulphide and carbon tetrachloride, the relation between con-

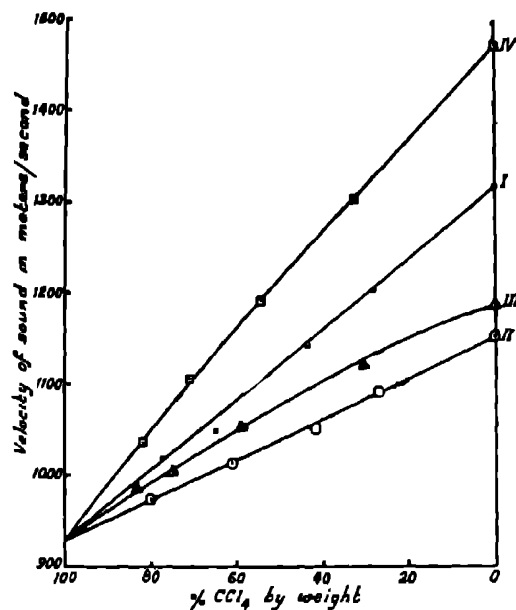


FIG. 2.

centration and sound velocity is strictly linear; while for the other two mixtures, the graphs are slightly concave towards the concentration axis, being much less so for tetralin and carbon tetrachloride, the mixture (4).

Fig. 3 shows that the graphs for the mixtures (a) CCl_4 and CS_2 and (b) CCl_4 and ethyl acetate are straight lines depicting strict linearity of adiabatic compressibility with concentration. That for benzene and CCl_4 is concave

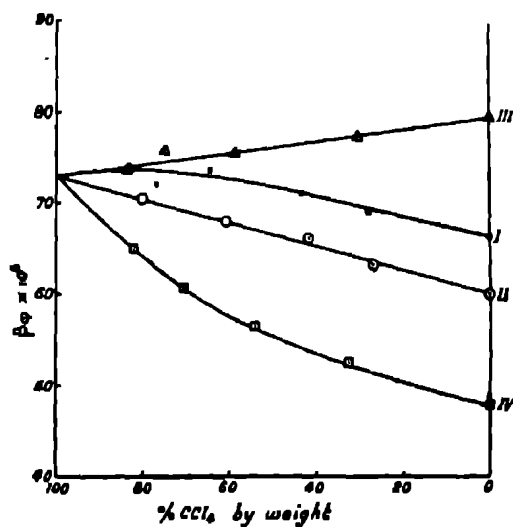


FIG. 3.

while the graph for CCl_4 and tetralin is convex towards the concentration axis.

These are explicable if we study the relationship between the density and concentration of these mixtures. For then here, the adiabatic compressibility has been calculated from both sound velocity and density, and is not a direct and separate determination.

From these results one can say that the sound velocities vary almost linearly with the concentration in the case of mixtures

In this connection, we may remark that when the author was studying² the light-scattering in liquid mixtures, he observed some anomalies. On plotting the concentration θ_1 of the mixture against the intensity of scattered light I, the author found that there were three typical kinds of curves :

- (1) the curve being concave towards the θ_1 axis , as in benzene and CCl_4 ;
- (2) the graph being a straight line ; as in ethyl acetate and CCl_4 ;
and
- (3) the curve being convex towards θ_1 axis ; as in CCl_4 and nitrobenzene, and CCl_4 and CS_2

We shall now compare the forms of curves in the two cases . (1) of intensity of scattered light to concentration of the earlier paper, and (2) the adiabatic compressibility with concentration contained in this paper . Of the four mixtures studied, three have been experimented on in both the papers.

(a) *Benzene and carbon tetrachloride*—The curve, the intensity of scattered light with concentration, has a form concave to the latter axis ; that is for intermediate positions, the intensity is greater . The adiabatic compressibility-concentration curve is also of the same form ; the compressibility is greater at intermediate concentrations . This is naturally to be expected as an increase in compressibility gives an increase in the intensity of scattered light.

(b) *Carbon disulphide and carbon tetrachloride*—The graph for this mixture in the light-scattering studies, takes an opposite shape to the case under (a), being very slightly convex towards the concentration axis. The course of the curve in compressibility-concentration is almost a straight line . But it must be remarked here that the changes observed are not great

(c) *Ethyl acetate and carbon tetrachloride*.—The graph was observed to be a straight line in the light-scattering studies, the relation between I and θ_1 being strictly proportional . Here also, the relation between the adiabatic

² S. Parthasarathy, *Ind Jour. Phys*, 1934, 7, 275

compressibility and concentration is linear, which explains the result in the earlier paper.

The mixtures studied in the light-scattering work were completely miscible and it is well known that in such cases, where one does not work near the critical solution temperature, the intensity of concentration-scattering is negligible compared to density and orientation scattering, which density scattering involves the compressibility. This is clear from the calculations shown in the author's paper on light-scattering on page 307. Hence we are justified in observing the changes in the curves as mainly due, if not wholly, to the compressibility not varying linearly with concentration.

It may be remarked here that this method of getting the values for the compressibilities of binary liquid mixtures has been useful in explaining some of the anomalies observed earlier, which otherwise would not have been possible.

It is known that in all the expressions for the intensity of scattered light, we are concerned with the isothermal compressibility β_T and not with β_ϕ . These two compressibilities are related together and is given by the expression:

$$\beta_T = \beta_\phi + \frac{\alpha^2 \tau}{J C_p d}$$

where α is the coefficient of thermal expansion,

C_p is the specific heat at constant pressure at absolute temperature T ,

J is the mechanical equivalent of heat, and

d is the density

so that any variation in β_ϕ will also affect β_T . In the expression on the right-hand side β_ϕ is large compared to the second term, and unless there are large variations in α and d , we can, without error, say that the course of the curves for both β_T and β_ϕ will be similar. Hence, we are not wrong in applying, at least qualitatively, the results of β_ϕ in mixtures to light-scattering experiments.

Since, in the formula given above, necessary data regarding α and C_p are lacking for the mixtures at different concentrations, we cannot fully work out the values for β_T for all these mixtures.

The author thanks Sir C. V. Raman, Kt., for the interest shown in this work.

Summary.

The paper gives results and graphs of (a) ultrasonic velocities and (b) adiabatic compressibilities in the following four binary liquid mixtures in all of which one component is carbon tetrachloride; the second component being (1) benzene, (2) carbon disulphide, (3) ethyl acetate and (4) tetralin.

The variation of adiabatic compressibility of the mixture was found to be not always strictly proportional to concentration. These results are applied to experimental investigations in an earlier paper of the author² where it was observed that the intensity of scattered light in binary liquid mixtures (completely miscible and at temperatures far removed from the critical solution temperature) was not always proportional to concentration. The trend of the curve in light-scattering and compressibility studies is the same, being concave or convex towards the concentration axis in both the cases, or being straight. The agreement is satisfactory

ON A FUNCTION CONNECTED WITH THE SINGULAR SERIES.

BY K. SAMBASIVA RAO.

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(Communicated by Dr. S. Chowla.)

NOTATION.

$$(1) \quad s_{\zeta} = \sum_{h=0}^{q-1} \zeta^{hn}$$

where, for integers $(a, q) = 1$, $\zeta = e^{2\pi i \frac{a}{q}}$ is a primitive q th root of unity and n is an integer ≥ 2 .

$$(2) \quad A_{n,s}(q, N) = q^{-s} \sum_{\zeta} (s_{\zeta})^s \zeta^{-N}$$

where the summation extends over all primitive q th roots, of unity, and N is an integer.

$$S = \sum_{q=0}^{\infty} A(q)$$

is known as the singular series. Also, it is known* that

$$S = \prod_p \chi_p$$

where p runs through all primes and

$$\chi_p = \sum_{l=0}^{\infty} A(p^l).$$

$M(p^l, N)$ denotes the number of solutions of $\sum_{\nu=1}^r h_{\nu}^n \equiv N \pmod{p^l}$, where $0 \leq h_{\nu} < p^l$.

$p^{\theta} \parallel N$ denotes that
 $p^{\theta} \mid N$ but $p^{\theta+1} \nmid N$.

It is known from the researches of Hardy and Littlewood that $A(p^l)$ vanishes for values of l on and after a certain stage. This is given as the

THEOREM I. If $p^{\beta} n + \sigma \parallel N$, then

$A(p^l) = 0$ for $l > \text{Max}(\beta_n + \sigma + 1, \beta_n + \gamma)$ where $0 \leq \sigma < n$ and $\gamma = \theta + 1$ for all $p > 2$, θ being defined by $p^{\theta} \parallel n$.

In the particular case when $p \nmid n$ (which is true after a certain point), this theorem becomes

* See Landau's *Vorlesungen über Zahlentheorie*, Band I, referred to, in this paper, at any subsequent time, as LVI.

THEOREM II. If $p^n + \sigma \nmid N$, $(p, n) = 1$, then $A(p^l) = 0$ for $l > \beta n + \sigma + 1$.

This note contains a very simple proof of the above proposition. For this purpose the following simple lemmas are needed

Lemma 1†. For $q = p^l$, $p \nmid n$, $2 \leq l \leq n$

$$s_\zeta = p^{l-1}$$

Lemma 2†. For $q = p^l$, $l > n$

$$s_\zeta = p^{n-1} s_{\zeta p^n}$$

Note ζp^n is a primitive $p^{(l-n)}$ th root of unity.

Lemma 3. If ζ is a primitive p^l th root of unity, then

$$\sum \zeta p^r = 0 \quad \text{whenever } l > r + 1, \text{ or, in other words,}$$

$$\zeta$$

$$\sum_{\substack{0 < a < p^l \\ (a, p^l) = 1}} e^{2\pi i \frac{a}{p^m}} = 0 \quad \text{whenever } 1 \leq m \leq l.$$

Proof:—

$$\sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{2\pi i \frac{a}{p^m}} = p^{l-m} \sum_{\substack{a < p^m \\ (a, p^m) = 1}} e^{2\pi i \frac{a}{p^m}}$$

Also, $e^{2\pi i \frac{a}{p^m}}$ for each $a < p^m$, $(a, p^m) = 1$, is a root of the equation

$$\frac{x^{p^m} - 1}{x^{p^{m-1}} - 1} = 0$$

The equation can be given as

$$x^{(p-1)p^{m-1}} + x^{(p-2)p^{m-1}} + \dots + 1 = 0$$

The sum of the roots of the above equation is zero for $m > 1$, since

$$(p-1)p^{m-1} > (p-2)p^{m-1} + 1.$$

This proves the lemma.

Proof of Theorem II.

Let $l = an + r$ where $0 < r \leq n$.

We have by Lemma 2

$$(A) \quad s_\zeta = p^{a(n-1)} s_{\zeta'},$$

where ζ' is a primitive p^r th root of unity, and $\zeta' = e^{2\pi i \frac{a}{p^r}}$. In the case when $r \neq 1$, from (A) and lemma 1 it follows that

$$\begin{aligned} s_\zeta &= p^{a(n-1)} p^{r-1} \\ &= p^{l-(a+1)}. \end{aligned}$$

† LVI, pp. 294 and 297.

Therefore

$$\begin{aligned} A(p^l) &= p^{-ls} \times p^{ls-s(a+1)} \sum_{\zeta} \zeta^{-n} \\ &= p^{-s(a+1)} \sum_{\zeta} \zeta^{-n}. \end{aligned}$$

But

$$(B) \quad \sum_{\zeta} \zeta^{-n} = \sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a}{p^l} N_0 p^{\beta n + \sigma}}$$

Where $N = N_0 p^{\beta n + \sigma}$ and $(N_0, p) = 1$.

Also when a runs through a reduced residue system mod p^l , so does $-N_0 \times a$. Therefore,

$$\begin{aligned} (C) \quad \sum_{\zeta} \zeta^{-n} &= \sum_{\substack{b < p^l \\ (b, p^l) = 1}} e^{\frac{2\pi i b}{p^l - (\beta n + \sigma)}} \\ &= 0 \text{ by lemma 3, whenever } l > \beta n + \sigma + 1. \end{aligned}$$

when $r = 1$, from (A) we have

$$\begin{aligned} A(p^l) &= p^{-ls+s a^{(n-1)}} \\ &\times \sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a N}{p^l}} \times \left(\sum_{h=0}^{p-1} e^{\frac{2\pi i a h^n}{p}} \right)^s \end{aligned}$$

But

$$\begin{aligned} &\sum_a e^{\frac{-2\pi i a N}{p^l}} \left(\sum_h e^{\frac{2\pi i a h^n}{p}} \right)^s \\ &= \sum_a e^{\frac{-2\pi i a N}{p^l}} \sum_{0 \leq h_v < p} e^{2\pi i \frac{a}{p} (h_1^n + \dots + h_s^n)} \\ &= \sum_a e^{\frac{-2\pi i a N}{p^l}} \sum_{t=0}^{p-1} M(p, t) e^{\frac{2\pi i a t}{p}} \\ &= \sum_{t=0}^{p-1} M(p, t) \sum_a e^{\frac{-2\pi i a N}{p^l}} \times e^{\frac{2\pi i a t}{p}}. \end{aligned}$$

But

$$\begin{aligned} &\sum_{\substack{a < p^l \\ (a, p^l) = 1}} e^{\frac{-2\pi i a N}{p^l}} \times e^{\frac{+2\pi i a t}{p}} \\ &= \sum_a e^{\frac{2\pi i a p^{\beta n + \sigma}}{p^l} - N_0 + t p^{(l - (\beta n + \sigma + 1))}} \\ &= 0 \end{aligned}$$

whenever $l > \beta n + \sigma + 1$ for reasons similar to those given for (B) and (C). Hence the proposition is proved.

THE RAMAN SPECTRUM AND ELECTROLYTIC DISSOCIATION OF SELENIC ACID.

BY C. S. VENKATESWARAN.

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received March 26, 1936

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

1 Introduction.

IN the previous communications to these *Proceedings*¹ the author has shown how a detailed study of the Raman spectra of weak acids like iodic and phosphoric acids yield information regarding the progressive electrolytic dissociation of these acids in aqueous solutions. The present paper deals with the results obtained in a similar investigation with selenic acid. The Raman spectrum of a strong solution of this acid has been studied by A. S. Ganesan² and he has reported five lines of frequency shifts* 315 (*m*), 422 (*m*), 730 (*f*), 850 (*s*), 926 (*f*) which differ in a marked manner from the shifts of the modified lines in selenates. A quantitative study of the Raman spectrum of this acid for a wide range of concentrations and a comparison of the results with those of sulphuric acid appear to be of great interest; for it could be expected to yield some information regarding the properties of similar compounds belonging to the same homologous series in the periodic system. The Raman spectra studies of sulphuric acid are numerous and though the results are vitiated to some extent by the presence of a strong continuous spectrum, there is general agreement among the several investigators regarding the evidence for the stepwise dissociation of this acid. In the case of selenic acid, as far as the author is aware of, there are no physico-chemical data available at present indicating its stages of ionisation. It can also be easily obtained in the crystalline form in which it exists as hundred per cent acid and it possesses a low melting point of about 50°·8 C. Hence it affords an interesting case of an acid in which the changes in position and character of the Raman lines could be followed up as it passes from solid to liquid and to solutions of varying concentration and the manner of electrolytic dissociation could be uniquely determined.

¹ Venkateswaran, C. S., *Proc Ind Acad. Sci.*, A, 1935, 2, 119; 1936, 3, 25.

² Ganesan, A. S., *Proc Ind. Acad. Sci.*, A, 1934, 1, 156

* The numbers in this and the subsequent pages denote the wavenumbers in cm⁻¹.

2 Experimental

The experimental set up for this investigation was the same as those described by the author in the previous communications ^{3,4} Hundred grams of pure crystalline selenic acid were supplied by Kahlbaum in a sealed tube and were used as such without further purification. Since the substance is highly hygroscopic, the sealed tube was kept intact during the investigation in the solid, molten and super-cooled states. The time of exposure for obtaining a satisfactory spectrogram was half an hour for the solid and twenty-four hours for the molten and the super-cooled liquid. In order to obtain a fairly quantitative estimate of the relative intensities of the lines in the aqueous solutions of varying concentration the product of the concentration and the time of exposure was kept constant, while the other conditions of experiment remained the same. The time of exposure for the 92.5% solution was twelve hours and was correspondingly increased for other concentrations. Specially backed Ilford "Golden Isozenith" plates were used for photographing the spectra. The plates were measured by means of a Hilger cross-slide microscope in comparison with an ion arc spectrum which was recorded in the centre of every picture.

3 Results

Enlarged photographs of the spectra are reproduced in the accompanying plates and illustrate the changes in the Raman lines during the transition from solid to liquid and to the aqueous solutions. The concentrations are given as percentages of the solid per hundred grams of the solution. The schematic representation of lines in Fig 1 shows clearly the changes in position and relative intensities of the lines as the dilution progresses. The thick dark lines are drawn with reference to a frequency scale in cm^{-1} units and their positions in the scale represent the frequency shifts corresponding to the maximum intensity of the banded Raman lines. The height of each dark line is proportional to the intensity of the corresponding modified line. The lines due to the same mode of vibration of the molecule in the different stages of dilution are joined together by dotted lines and their assignment is indicated below.

³ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1935, 1, 850; *loc. cit.*

⁴ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1936, 3, 25.

TABLE I. (*Selenic acid.*)
Raman frequencies in cm^{-1} .

State of Substance	1	2	3	4	5	6	7	8	9	10	11	12
Crystal	1383 (1)	..	930 (4) sh.	896 (5) sh.	..	778 (1)	766 (5) sh.	374 (2) sh.	355 (1) sh.	327 (1) sh.
Molten	..	1186 } (0) 1105 }	996 (3) 36	914 (8) 70	756 (10) 70	388 (6) 40	361 (6) 40	294 (3) 40
Super-cooled	978 (2) 32	899 (8) 30	752 (10) 30	387 (3) 16	360 (3) 16	294 (3) 20
92.5	..	1160 (0) band	975 (1) 12	927 (2) 16	..	862 (5) 20	747 (10) 30	..	374 (5) 60	299 (5) 30
75	934 (3) 20	..	826 (8) 16	748 (6) 20	..	390 (3) 50	307 (4) 30
50	929 (3)	..	862 (10) 16	845 (0) sh.	..	742 (3) 20	..	390 (3) 40	312 (3) 30
30	929 (2)	910 (0)	866 (10)	846 (1)	..	737 (3) 20	..	390 (3) 30	327 (3) 30
20	925 (2)	908 (2)	866 (8)	845 (2)	..	732 (2) 20	..	398 (3) 20	332 (3) 20
15	921 (1)	908 (2)	866 (8)	845 (4)	..	732 (1) 20	..	400 (3) 16	332 (3) 20
7.5	921 (0)	908 (1)	866 (6)	845 (3)	..	732 (0) 20	..	402 (1) 16	332 (1) 20

▼ *Note.*—The numbers within the brackets indicate visual estimate of intensities and the numbers below each frequency give the breadth of the line in cm^{-1} .

Table I gives the frequency shifts of the centre of the Raman lines of the acid as solid, liquid and aqueous solutions of concentrations ranging from 92.5% to 7.5% by weight. Visual estimates of the intensities of the lines are given within brackets accompanying the corresponding line. The extension of the line to either side of its centre is given in wavenumber units below the frequency values.

4. Discussion of Results

The Raman spectrum of the crystalline selenic acid consists of seven sharp lines of frequencies 930 ($\frac{1}{2}$), 896 (5), 778 (1), 766 (5), 374 (2), 355 (1)

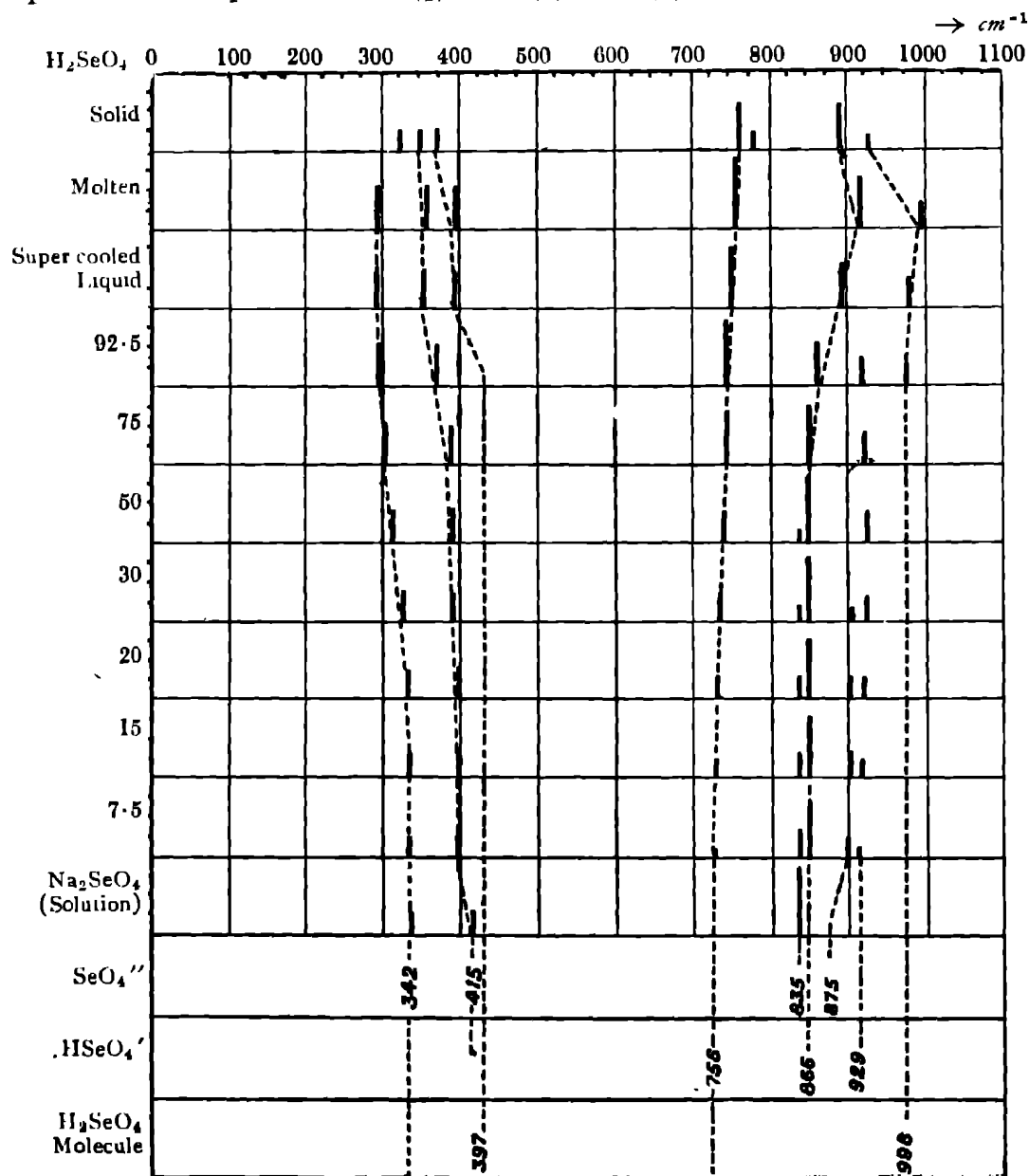


FIG. 1.

and 327 (1). Though the slit width employed throughout the experiment was a minimum (about $1/50$ mm.), all the lines in the solid broaden out in the liquid and the solutions of high concentrations and tend to become sharper as the dilution increases. The lines undergo relative positional changes as can be inferred from the dotted lines indicating the course of each line in Fig. 1.

On melting the solid, the weak line 930 becomes a band of about 36 wavenumbers in width and undergoes a maximum shift of 66 wavenumbers towards higher frequency. In the super-cooled liquid this line as well as the other lines tend to approach that of the solid. The addition of a small quantity of water to the acid diminishes its intensity considerably and the frequency shift is also less than in the liquid state. At 75% this line practically disappears. But, instead, a new band makes its appearance first at 92.5% with a frequency shift of about 927 and increases in intensity from 92.5% to 30%. The centre of the line undergoes a gradual shift towards shorter frequency as dilution increases. At about 30% concentration this band at 927 shows a distinct doublet structure and for the lower concentrations it shows a clear asymmetry in intensity, the shorter frequency side increasing and the longer frequency side decreasing gradually in intensity. This is interpreted as due to the appearance of a new line at 910 at about 30% concentration, which is probably also present weakly at higher concentrations and which accounts for the apparent frequency shift of the line. The new line at 910 possesses a fairly constant frequency.

The line 896 which is one of the two intense lines in the solid phase has a finite breadth, but becomes very much broader (about 70 wavenumbers) and shifts towards a higher frequency of 914 in the liquid. The structure of this band is, however, different from that of the rest in the spectrum. It consists of a fairly broad line of maximum intensity at the centre and followed on either side by rotation wings. On the addition of water this line undergoes a marked change both in structure and position. In the 92.5% solution, it has only a breadth of about 20 wavenumbers. The frequency corresponding to maximum intensity is 862, thus undergoing a change of about 50 wavenumbers towards shorter frequency from the liquid to the solution. It has a constant frequency at all dilutions and becomes sharper at lower concentrations. The changes of intensity of this line are very striking. At 92.5% it is only half as intense as the one at 747; but at 75% its intensity is already slightly greater than that of the latter and goes on increasing up to about 30%. Though it continues to be the most intense line at lower concentrations, it appears to lose in intensity on further dilution. At

about 30% a new sharp line begins to make its appearance at 845 and gains in intensity as the dilution progresses.

The intense line at 766 and its faint companion at 778 of the solid appear as a single broad line (about 70 wavenumbers) in the molten state as well as at all dilutions. But this band changes in position progressively towards smaller frequency both during the transition from the solid to the liquid and on the addition of more and more of water. It appears as the most intense line in the liquid and in the solution of 92.5% concentration, but rapidly loses its intensity with dilution. At about 7.5% it is very faint and difficult to measure though it remains fairly broad. The extraordinary breadth of this line even at the highest dilution can be interpreted as due to the superposition of two diffuse lines, which in the solid show themselves as sharp lines. The change in the relative intensities of the two components also probably account to some extent for the frequency changes of the band towards the stronger line.

The two low frequencies at 274 and 355 in the solid state preserve the doublet character in the molten liquid, but in the solution appear as a single broad band (about 60 wavenumbers) which is asymmetrical in structure, being more intense towards shorter wavelength. The changes in the asymmetry of its structure in the solutions, however, show that the higher frequency component diminishes rapidly in intensity. The third low frequency at 327 in the solid, on the other hand, undergoes a degradation in frequency from the solid to liquid and becomes broad. It has almost the same frequency value at 92.5% solution as in liquid, but gradually increases towards higher frequency as the dilution progresses in the same manner as the band at 390. Though up to about 50% concentration the 390 band is broader than the one at 312, they are almost equal at 30% and at lower concentrations, there is a complete reversal in the relation between the widths of these two bands.

TABLE II. (*Sulphuric acid.*)
Raman frequencies in cm^{-1} .

Concentration	1	2	3	4	5	6	7	8	9
100 %	..	562	911 (6) 30	1142
90 %	..	408 (3) 60	565 (4) 60	911 (5) 35	970 (0)	1038 (4) 40
75 %	..	418 (3) 60	579 (4) 60	905 (4) 40	..	1034 (5) 40
50 %	..	426 (3) 60	588 (4) 60	897 (3) 50	..	1038 (5) 40	1172	1234	1341
30 %	..	427 (3) 60	593 (4) 60	896 (2) 55	..	1047 (6) 30	1172	1223	1334
20 %	..	429 (3) 60	592 (4) 60	895 (0) 60	..	1050 (6) 25	1168	1236	faint
10 %	..	faint	592 (4) 60	895 (0) 60	..	1051 (6) 20

Besides these lines there is one line at 1383 in the solid and two diffuse lines at 1186 and 1105 in the liquid which appear as a broad band at 92.5% concentration.

The characteristic Raman band of water begins to show at 75% and gains rapidly in intensity as the dilution progresses. The triple structure of the band is difficult to identify but the relative intensities of the different portions of the unsymmetrical band agree fairly closely with that of pure water itself.

5. Comparison with Sulphuric Acid.

It is known that selenic acid is a strong acid comparable in strength with its analogue, sulphuric acid and it is to be expected that it should show an anomalous behaviour in its Raman spectra similar to that of the latter. The above picture of the changes in position, intensity and structure of the Raman lines, corresponds closely with similar observations by previous investigators⁵ in sulphuric acid. For purposes of comparison the Raman frequencies of sulphuric acid solutions are reproduced in Table II from an exhaustive study of this acid by Bell and Jeppesen.⁶ In general, the Raman spectra of the different solutions of this acid consists of four sets of lines namely,

(1) 911–895 and 1142 which are present in the 100% acid and drop off in intensity as it is diluted ; these are assigned to the undissociated molecules

(2) 1038–1051 which is not present in the pure acid but which appears and rapidly becomes stronger on dilution , this is attributed to HSO_4' ions.

(3) 982 which though present in 50% and perhaps also in 75% becomes appreciable only at concentrations lower than 25% ; this is characteristic of the SO_4'' ions.

(4) Those at 408–429 and 562–592 which are present at all concentrations and seem to belong to the ions and molecules alike

Our results with selenic acid can also be classified as above.

(1) The lines 756–732, 996–976, 388–397 and 1186–1160 are present in the liquid and in 92.5% solution, but either totally disappear or drop off in intensity as the dilution increases. It is interesting to observe that the most intense line in this group, namely, 756–732 undergoes a shift towards a lower frequency just as the corresponding line 911–895 in the sulphuric acid.

(2) The lines 862 and 927–921 rapidly increase in intensity up to about 30% and remain intense throughout.

⁵ For complete references, see Angus and Leckie, *P.R.S*, 1934, **149A**, 327

⁶ Bell, R. M., and Jeppesen, M. A., *J. Chem. Phys*, 1935, **3**, 245

(3) The lines 908 and 845 begin to appear faintly at about 50% and increase in intensity on further dilution. Unlike the corresponding line 982 of sulphuric acid, the line 845 never becomes a prominent line in the spectrum.

(4) The broad lines 360-402 and 294-332 are present at all concentrations as well as in the solid. They behave exactly like the lines 562-592 and 408-429 in sulphuric acid as regards positional changes

There is, thus a close correspondence between the two spectra, the corresponding frequencies themselves being smaller in selenic acid as is to be expected because of the greater atomic weight of selenium

Recently there has been a controversy regarding the frequency shifts of some of the lines in sulphuric acid. Woodward and Horner⁷ have pointed out that the apparent shifts could be interpreted on the basis that the broad lines consist of components of slightly different frequencies which appear and disappear at different concentrations. Bell and Jeppesen,⁸ however, disagree with the above authors and insist that the lines are symmetrical, and the shift is gradual and depends on the influence of the state of solution on the vibrations of the molecular species concerned.

As has been pointed out before, our results with selenic acid support the view put forward by Woodward and Horner regarding the composite nature of the broad lines. The bands in the selenic acid which undergo frequency variations show a doublet nature at a particular concentration and a marked asymmetry in their structure at other dilutions. In the solid, the corresponding lines are generally split up. The only exception to this is the low frequency at about 300. These observations were possible in the spectra of this acid because of the clearness of the picture in all states. But in the case of sulphuric acid, a strong continuous spectrum obscures finer details. In view of the close accordance between the results of selenic acid and sulphuric acid in other respects, it seems probable that in the case of the latter also the diffuse Raman lines consist of relatively narrow components as suggested by Woodward and Horner. It should, however, be pointed out that the complete drift of the lines due to changing concentrations could not be accounted for mainly on the basis of components.

6. Electrolytic Dissociation of Selenic Acid.

From what has been stated in the previous section, it will be clear that the anomalous variation in intensity and frequency shifts that are observed in the Raman lines in selenic acid could be explained in the same manner as in the case of sulphuric acid, namely, by assuming that this acid, like the

⁷ Woodward and Horner, *Proc Roy Soc., A*, 1934, **144**, 129.

⁸ Bell, R. M., and Jeppesen, M. A., *loc. cit.*

latter ionises in two stages, first from $\text{H}_2\text{SeO}_4 \rightarrow \text{HSeO}_4' + \text{H}^\circ$ and then from $\text{HSeO}_4' \rightarrow \text{SeO}_4'' + \text{H}^\circ$. On the basis of this hypothesis the band 756–732 which is prominent in the molten condition and falls off in intensity gradually in aqueous solutions, is characteristic of the undissociated molecules. The lines with frequency shifts of 1186, 1105, 996–976 and 388 which are present only at 100% liquid and 92.5% solution also arise from the H_2SeO_4 molecules. The second intense line at 862 which gains rapidly in intensity as the concentration falls from 92.5% to 30% and the line at 927 are to be attributed to the first ionisation product, HSeO_4' ions. The frequency shifts observed for KHSeO_4^9 are 852 and 339. The close agreement between the line 852 in the biselenate and 862 assigned to HSeO_4' ion lends support to the above conclusion. Its presence in the 100% acid shows that, as is not the case with sulphuric acid, a certain proportion of molecules in the solid and the liquid states has undergone partial dissociation from H_2SeO_4 to HSeO_4' . The great intensity of this line in most of the concentrations is due to the preponderance over all others of the HSeO_4' ions which give rise to it and shows its remarkable stability in the aqueous solutions. The line at 845 which makes its appearance first at 50% and gains steadily in intensity on further dilution, as well as the line at 908 are to be attributed to the normal vibrations of the SeO_4'' ions. This indicates that the second stage of ionisation from $\text{HSeO}_4' \rightarrow \text{SeO}_4'' + \text{H}^\circ$ begins only at 50% and even at 7.5% it is not appreciable. The two low frequencies 361–402 and 294–332 appear to be common to all the three molecular species.

In Table III the frequencies assigned to SeO_4'' and SO_4'' ions in the acids are compared with the corresponding frequencies in selenates¹⁰ and sulphates¹¹ respectively.

TABLE III.

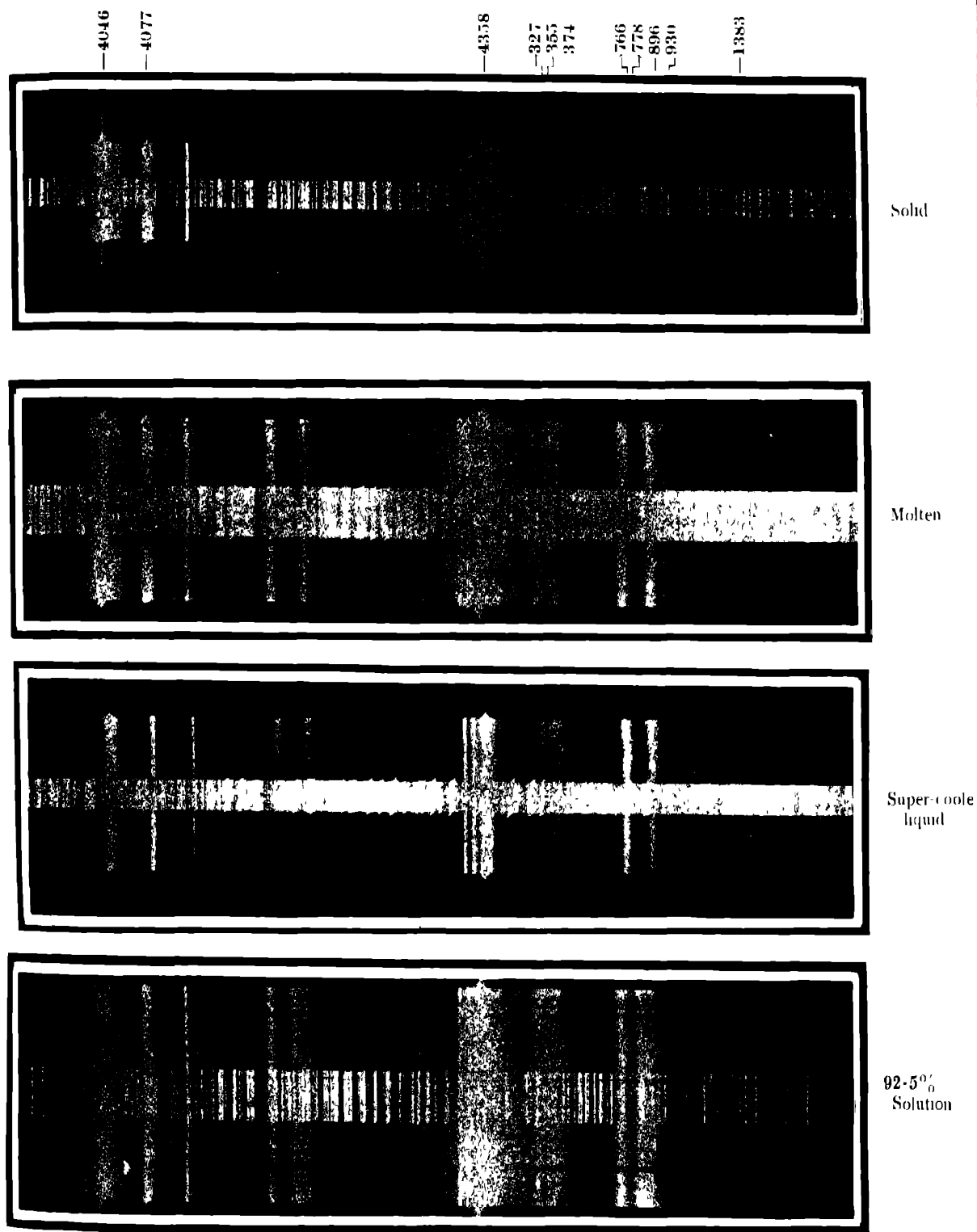
SeO_4'' (in 7.5% acid)	..	332	402	845	908
SeO_4'' (in Selenate)	..	342	415	835	875
SO_4'' (in 10% acid)	..	418	597	982	1168
SO_4'' (in Sulphate) ^o	.	447	623	983	1115

It is interesting to note a systematic variation in frequencies in both SeO_4'' and SO_4'' ions while passing from the acid to the salt. The close agreement between the values of the Raman lines arising from SeO_4'' in the acid and the selenates, lends support to the above interpretation of the results. The

^o Pringsheim and Yost, *Zeit. f. Physik*, 1929, **58**, 1.

¹⁰ A. S. Ganesan, *loc. cit*

¹¹ Kohlrausch, *Der Smekal-Raman Effect*, 1931.



Raman Spectra of Selenic Acid
(Solid, Liquid and Solution).

presence of the line at 732 even at 7.5% solution shows that a certain proportion of the H_2SeO_4 molecules exists even at those dilutions. It is very difficult to say whether the $\text{SeO}_4^{''}$ ions are produced by the direct dissociation of H_2SeO_4 to 2H^+ and $\text{SeO}_4^{''}$ or only from the first ionisation product HSeO_4' which appears to be very stable. In general, the results indicate that selenic acid possesses a lower degree of ionisation than sulphuric acid.

The absence of any line in the spectrum of selenic acid at about 2312 corresponding to the Raman line in liquid hydrogen selenide¹² signifies that no H-Se bond is present in the molecule.

7. *Change of State and Raman Effect.*

The influence of change of state from the solid to liquid on the Raman lines of this acid is illustrated in the accompanying plate. Two distinct changes occur on the lines, namely, a shift towards longer wavelength of all the lines except 766 and 327 which have a reverse effect and a general broadening. In the super-cooled liquid these effects are, to some extent, less pronounced. In general, these changes of the lines following the change of state are characteristic of hetro-polar compounds.¹³ Their full significance will be discussed in a separate paper along with the results of selenious acid.*

In conclusion the author wishes to express his thanks to Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectrum of selenic acid has been investigated in the state of solid, liquid and aqueous solutions of concentrations varying from 92.5% to 7.5% by weight. The solid has yielded eight lines with frequency values of 1383, 930, 896, 778, 766, 374, 355 and 327. Marked changes in position, intensity and character of these lines are observed during the transition from the solid to the liquid and then to the aqueous solutions. The gradual disappearance of some of the lines and the increase in the intensity of some others and the appearance of new lines are explained on the basis of the stepwise dissociation of the acid, namely, $\text{H}_2\text{SeO}_4 \rightarrow \text{HSeO}_4' + \text{H}^+$ and $\text{HSeO}_4' \rightarrow \text{SeO}_4^{''} + \text{H}^+$. The results indicate that the first stage of ionisation starts from the solid and the second stage from about 50% concentration. The results are compared with those of its analogue, sulphuric acid and conclusions are drawn regarding the structure and the apparent shifts of the bands in both these acids. The changes that take place in the lines during the transition from the solid to the liquid are characteristic of the hetro-polar nature of the chemical bond in the acid molecules.

¹² Dadiou and Engler, *Wien Anz*, 1935

¹³ Venkateswaran, C. S., *Proc. Ind Acad Sci., A*, 1935, 2, 260.

* Unpublished work of the author.

THE NEUTRINO THEORY OF LIGHT.

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1. Introduction.

THE most important contribution during the last years to the fundamental conceptions of theoretical physics seems to be the development of a new theory of light which contains the acknowledged one as a limiting case, but connects the optical phenomena with those of a very different kind, radio-activity. The idea that the photon is not an elementary particle but a secondary one, composed of simpler particles, has been first mentioned by P. Jordan¹. His argument was a statistical one, based on the fact, that photons satisfy the Bose-Einstein statistics. It is known from the theory of composed particles as nuclei, atoms or molecules, that this statistics may appear for such systems, which are compounds of elementary particles satisfying the Fermi-Dirac statistics (*e.g.*, electrons or protons). After the discovery of the neutrino, de Broglie² suggested that a photon $h\nu$ is composed of a "neutrino" and an "anti-neutrino," each having the energy $\frac{1}{2}h\nu$. He has developed some interesting mathematical relations between the wave equation of a neutrino (which he assumed to be Dirac's equation for a vanishingly small rest-mass) and Maxwell's field equations. But de Broglie has not touched the central problem, namely, as to how the Bose-Einstein statistics of the photons arises from the Fermi-statistics of the neutrinos. This question cannot be solved in the same way as in the cases mentioned above (material particles) where it is a consequence of considering the composed system as a whole neglecting internal motions. This is possible because of the strong forces keeping the primary particles together. But in the case of neutrinos we have no knowledge of such forces, and it would contradict the simplicity of de Broglie's idea to introduce them.

¹ P. Jordan, "Die Lichtquanten hypothese," *Erg der Exakt. Naturw.*, 1928, 17, 158.

P. Jordan, *Zeits. f. Phys.*, 1935, 93, 464; 1936, 98, 709 and 759; 1936, 99, 109.

² L. de Broglie, *C.R.*, 1932, 195, 536, 577, 862; 1933, 197, 1377; 1934, 198, 135; 1934, 199, 445, 1165. A coherent representation is to be found in his book *Une Nouvelle Conception de la Lumiere* (181, Act. Sci. et Ind.) Further L. de Broglie and J. Winter, *C.R.*, 1934, 199, 813.

This fundamental problem has been solved by Jordan. He has shown that no forces between neutrinos are required but the way of their interaction with electric charges leads to the effect that pairs of neutrinos behave generally as photons. Jordan has formulated the principles involved and has proved rather deep mathematical theorems expressing the relation of neutrinos and photons. The fuller development of the mathematical method is due to R. de L. Kronig³ who is working in close co-operation with Jordan. We shall give here a report on the present situation, as far as it has come to our knowledge and hope that this will be welcome to the readers, not only because the original papers are scattered over several periodicals but are extremely difficult to read as they contain some apparent contradictions which have not been avoided even in the latest paper.

We disagree with Jordan and Kronig only in one essential point. It is that we see no reason to introduce the spin of the neutrino, but that we can describe the difference between the two kinds of neutrinos in the same way as the difference between electrons and positrons in Dirac's theory of holes.

We have tried to make this report comprehensive without much recourse to literature.

2. *The Neutrino.*

The particles which physics considers to-day as elementary can be ordered corresponding to their masses in 3 groups, each containing two types :

1. Particles of great mass : proton, neutron ;
2. Particles of small mass : electron, positron ;
3. Particles of zero mass : photon, neutrino.

The central problem of future physics is the explanation of the existence of these different types of particles and the derivation of their properties from a fundamental principle. As to the first two groups, we think that the solution must lie in the direction of a non-linear field theory, as has been tried to develop.⁴ But the particles of the third group correspond classically to the case of very weak field, where the non-linearity plays no rôle. This limiting case was generally assumed to be known with any desired accuracy, as represented by the quantised field equations of Maxwell. But the discovery of the neutron has shaken this conviction and we are compelled to revise the very principles even of the limiting case, before we can hope to tackle the (probably non-linear) laws governing the higher particles.

³ R. de L. Kronig, *Physica*, 1935, 2, 491, 854, 968.

⁴ M. Born, *Proc. Roy Soc*, (A), 1934, 143, 410.

The experimental facts which lead Pauli to the assumption of neutrinos are connected with the β -decay of radio-active nuclei. The spectrum of the emitted electrons (or positrons in the case of induced radio-activity) is continuous and has a wide range of velocity. But the emitting nucleus and the resulting nucleus are in every respect definite systems. All attempts to account for this fact by a simultaneous emission of γ -rays have failed.

There are only two ways of explanation: either the law of the conservation of energy does not hold in these cases or there are particles emitted which cannot be detected by our experimental methods, because of their extreme penetrating power.

To avoid the first unpleasant alternative,* Pauli has put forward the idea that very light, uncharged particles are emitted simultaneously with the electron when a neutron is converted into a proton (or *vice versa*), and he has called them *neutrinos*. It is not quite hopeless to prove their existence by using very light atoms made radio-active with the help of Fermi's method of neutron bombardment. One could observe the recoil of these atoms when emitting the electrons and measure the energy and momentum of both the particles. If there is a third particle involved in the process, its energy E and momentum p should be connected by the relativistic relation $\frac{E^2}{c^2} - p^2 = m_0^2 c^2$ where c is the velocity of light and m_0 its rest-mass. If m_0 turns out to be constant (for instance zero), there could be no doubt about the existence of the neutrino. Experiments of this kind have been undertaken in the Cavendish laboratory at Cambridge.⁵

Fermi⁶ has shown that the hypothesis of neutrino emission for β -decay together with some simple and natural assumption about the interaction energy leads to a definite law of distribution for the emitted β -rays which is in good agreement with observation, if the rest-mass of the neutrino is taken as very small, very much smaller than that of the electron. It seems very probable that the rest-mass is exactly zero just as that of the photon.

These meagre facts are the experimental evidence on which the neutrino theory of light is based. *The leading idea is that the neutrinos are the primary*

* New experimental results of R. S. Shankland (*Phy Rev*, 1936, **49**, 8) on the Compton Effect (simultaneous emission of photons and electrons) indicate a failure of the conservation laws. P. A. M. Dirac has, therefore, concluded (*Nature*, 1936, **137**, 298) that the said laws have to be given up. Nevertheless, we think it worth while to study carefully the possible way out of this dilemma pointed out by the neutrino theory.

⁵ Bainbridge [*Science*, 1936, **83**, 38 (Suppl.)] claims to have a direct proof of the existence of the neutrino from considerations about the stability of isotopes.

⁶ E. Fermi, *Nuovo Cimento*, 1934, **11**, 1

particles moving with the velocity of light, and that the processes usually described in terms of photons or light waves are really simultaneous actions of several neutrinos.

Jordan and de Kronig have followed de Broglie in the assumption that there are two kinds of neutrinos, neutrinos and anti-neutrinos, differing by their spin. This is the only point where we do not agree with them. *We have found that the whole theory could be developed by assuming only one kind of neutrino which can have positive or negative energy.* Since in the thermal equilibrium at absolute zero all negative states are occupied, the total negative energy becomes infinite. This inconvenience is overcome by using the number of unoccupied states as variables and to call them anti-neutrinos, just as in Dirac's theory of holes representing positrons. But whereas in the case of the electrons, the formulation of this theory of holes leads to great difficulties,⁷ arising from the external fields which have to be taken into account, it is very simple and satisfactory here in the case of the neutrinos which are not attacked by external forces.

3. Fermi Statistics of Neutrinos.

We describe the motion of the neutrinos and anti-neutrinos with the help of two infinite sets of non-commuting variables α_κ , γ_κ which we numerate (for sake of convenience) with the help of half numbers, $\kappa = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. We define the α_κ , γ_κ also for negative indices with the help of the relations:*

$$(1) \quad \alpha_{-\kappa} = \gamma_\kappa^\dagger; \quad \gamma_{-\kappa} = \alpha_\kappa^\dagger, \quad \kappa > 0$$

where the \dagger means the adjoint operator.

The meaning of these variables can be described, using the correspondence principle, as Fourier-coefficients of wave functions; for instance in one dimension

$$(2) \quad \begin{cases} \psi(t - x/c) = \sum_{\kappa=-\infty}^{\infty} \alpha_\kappa e^{2\pi i \nu_1 \kappa (t - x/c)}, \\ \chi(t - x/c) = \sum_{\kappa=-\infty}^{\infty} \gamma_\kappa e^{2\pi i \nu_1 \kappa (t - x/c)} = \psi^\dagger, \end{cases}$$

where ν_1 corresponds to the fundamental frequency of the waves in the finite space considered (Hohlraum). We can interpret κ as the positive or negative energy of the corresponding state in units of $h\nu_1$.

⁷ W. Heisenberg, *Zeits. f. Phys.*, 1934, 90, 209, and 1936, 98, 714.

P. A. M. Dirac, *Proc. Camb. Phil. Soc.*, 1934, 45, 245; and *Quantum Mechanics*, 1935, Chap. 13.

* There is really no use of using two kinds of variables, we introduce the γ_κ only to be in conformity with Jordan and to have symmetry between neutrinos and anti-neutrinos.

The functions ψ , χ are not self-adjoint ; but $\chi = \psi^\dagger$. Instead of using the states of negative energy, one can introduce the holes amidst the states ; the wave function describing them is $\chi = \psi^\dagger$ and to each positive energy κ belongs a neutrino (ψ , or a_κ) and a hole or anti-neutrino (χ or γ_κ).

We postulate the following commutation laws :

$$(3) \quad \begin{cases} a_\kappa a_\mu + a_\mu a_\kappa = 0 \\ \gamma_\kappa \gamma_\mu + \gamma_\mu \gamma_\kappa = 0 \\ \gamma_\kappa a_\mu + a_\mu \gamma_\kappa = \delta_{\mu, -\kappa} \end{cases}$$

The number of neutrinos and anti-neutrinos of energy κ is defined only for $\kappa > 0$ by the operators

$$(4) \quad \begin{cases} N_{\kappa}^{(+)} = a_\kappa^\dagger a_\kappa = 1 - a_\kappa a_\kappa^\dagger \\ N_{\kappa}^{(-)} = \gamma_\kappa^\dagger \gamma_\kappa = 1 - \gamma_\kappa \gamma_\kappa^\dagger. \end{cases}$$

There are two other expressions for each of these quantities with the help of (1)

It is well known that these operators (4) have only the eigenvalues 0, 1, which mean unoccupied or occupied state. As we do not suppose extended knowledge of literature, we shall explain this a little closer in the next section.

4 Matrix Representation of the Fundamental Operators.

We start with a simple case and define the matrices*

$$(5) \quad a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad a^\dagger = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}; \quad \text{and } s = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix};$$

which satisfy the following relations :

$$(6) \quad \begin{cases} a^2 = 0 & a^{\dagger 2} = 0 & s^2 = 1 \\ a^\dagger a + a a^\dagger = 1 & a s + s a = 0 & a^\dagger s + s a^\dagger = 0. \end{cases}$$

The matrix a is useful to describe a system with one state which could be occupied by a particle or not. We define the " number of particles " in this state which is of course either 0 or 1, with the help of the matrix

$$(7) \quad a^\dagger a = n = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix},$$

which is diagonal and has the eigenvalues 0 and 1.

Thus from (5) it follows that

$$(8) \quad a a^\dagger = 1 - n.$$

We remark that one has

$$(9) \quad s = 1 - 2n$$

but we do not enter in a more elaborate discussion of the interesting formalism connected with these matrices. Now we extend this method to systems with

* They are closely connected with Pauli's spin matrices

$\sigma_x = a^\dagger + a$; $\sigma_y = i(a^\dagger - a)$; and $\sigma_z = s$.

more than one state, occupied or not, by introducing the notion of the direct product of matrices.

5. Direct Product of Matrices

If $a = (a_{kl})$ and $b = (b_{mn})$ are two matrices, the direct product is given by

$$(10) \quad a \times b = (a_{kl} \cdot b_{mn})$$

i.e., the elements are all products of any element of a with any element of b .

$$(11) \quad (a \times b)_{km, ln} = a_{kl} b_{mn}.$$

If $a \times b = 0$ it follows that either $a = 0$ or $b = 0$.

Further

$$(12) \quad (a \times b)^+ = \{(a \times b)_{ln, km}^+\} = (a_{lk}^+ b_{nm}^+) = a^+ \times b^+.$$

6 Representation of a_κ and γ_κ .

We now give a representation of the matrices a_κ and γ_κ fulfilling (3) with the help of the direct products of matrices consisting of the fundamental matrices a and s . This representation was discovered by Jordan and Wigner⁸ who have also shown that the solution is unique apart from unitary transformations. Their representation is given by the scheme (next page).

Using the definition (10) of the direct product of matrices and the equations (6), (11) and (12), it can be easily verified that the representations of the fundamental operators given in (13) satisfy the commutation rules (3).

7. A New Set of Operators a_κ and c_κ .

We will now define, as Jordan has done, a new set of operators as functions of our fundamental operators a_κ and γ_κ .

They are

$$(15) \quad \begin{aligned} a_\kappa &= \frac{a_\kappa + \gamma_\kappa}{\sqrt{2}}, \\ c_\kappa &= \frac{a_\kappa - \gamma_\kappa}{i\sqrt{2}}. \end{aligned}$$

From (15) we can express a_κ and γ_κ as functions of a_κ and c_κ :

$$(16) \quad \begin{aligned} a_\kappa &= \frac{a_\kappa + ic_\kappa}{\sqrt{2}}, \\ \gamma_\kappa &= \frac{a_\kappa - ic_\kappa}{\sqrt{2}}. \end{aligned}$$

From (15) and (1) we see that

$$(17) \quad \begin{aligned} a_{-\kappa} &= \frac{a_{-\kappa} + \gamma_{-\kappa}}{\sqrt{2}} = \frac{\gamma_\kappa^+ + a_\kappa^+}{\sqrt{2}} = a_\kappa^+, \\ \kappa > 0 \quad c_{-\kappa} &= \frac{a_{-\kappa} - \gamma_{-\kappa}}{i\sqrt{2}} = \frac{\gamma_\kappa^+ - a_\kappa^+}{i\sqrt{2}} = c_\kappa^+. \end{aligned}$$

⁸ P. Jordan and E. Wigner, *Zets. f. Phys.*, 1928, 47, 631.

$$\begin{array}{c}
 (13) \\
 \kappa > 0
 \end{array}
 \begin{array}{c}
 a_{\kappa} = \gamma_{-\kappa}^{\dagger} \\
 a_{-\kappa} = \gamma_{\kappa}^{\dagger} \\
 \gamma_{\kappa} = a_{-\kappa}^{\dagger} \\
 \gamma_{-\kappa} = a_{\kappa}^{\dagger}
 \end{array}
 \begin{array}{c}
 \frac{1}{2}, -\frac{1}{2}, \frac{3}{2}, -\frac{3}{2}, \dots, (\kappa-1), -(\kappa-1), \kappa, -\kappa, (\kappa+1), -(\kappa+1), \dots
 \end{array}
 \begin{array}{c}
 s \times s \times s \times s \times \dots \times s \times s \times a \times 1 \times 1 \times 1 \times \dots \\
 s \times s \times s \times s \times \dots \times s \times s \times a^{\dagger} \times 1 \times 1 \times 1 \times \dots \\
 s \times s \times s \times s \times \dots \times s \times s \times a \times 1 \times 1 \times 1 \times \dots \\
 s \times s \times s \times s \times \dots \times s \times s \times a^{\dagger} \times 1 \times 1 \times 1 \times \dots
 \end{array}$$

Each matrix has only one non-vanishing element given by the following scheme in which t_{κ} is equal to zero or unity.

$$(14) \quad \left\{ \begin{array}{l}
 a_{\kappa} (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, 0, t_{-\kappa}, \dots, t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, 1, t_{-\kappa}, \dots) = (-)^{t_{\frac{1}{2}} + t_{-\frac{1}{2}} + \dots + t_{-(\kappa-1)}} \\
 a_{-\kappa} (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, t_{\kappa}, 1, \dots, t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, t_{\kappa}, 0, \dots) = (-)^{t_{\frac{1}{2}} + t_{-\frac{1}{2}} + \dots + t_{\kappa}} \\
 \gamma_{\kappa} (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, t_{\kappa}, 0, \dots, t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, t_{\kappa}, 1, \dots) = (-)^{t_{\frac{1}{2}} + t_{-\frac{1}{2}} + \dots + t_{\kappa}} \\
 \gamma_{-\kappa} (t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, 1, t_{-\kappa}, \dots, t_{\frac{1}{2}}, t_{-\frac{1}{2}}, \dots, 0, t_{-\kappa}, \dots) = (-)^{t_{\frac{1}{2}} + t_{-\frac{1}{2}} + \dots + t_{-(\kappa-1)}}
 \end{array} \right.$$

From (15) and (3), we obtain the commutation rules for the operators a_{κ} and c_{κ} .

$$(18) \quad \begin{aligned} a_{\kappa} a_{\mu} + a_{\mu} a_{\kappa} &= \delta_{\mu, -\kappa}; \\ c_{\kappa} c_{\mu} + c_{\mu} c_{\kappa} &= \delta_{\mu, -\kappa}; \\ a_{\kappa} c_{\mu} + c_{\mu} a_{\kappa} &= 0; \end{aligned}$$

for $\kappa, \mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \dots$

As the new operators a_{κ} and c_{κ} obey the commutation rules (18), a Jordan-Wigner representation can be developed for them. Thus $a_{-\kappa} a_{\kappa}$ or $a_{\kappa}^{\dagger} a_{\kappa}$ has the eigenvalues 0 and unity. Similar is the case of $c_{-\kappa} c_{\kappa}$ or $c_{\kappa}^{\dagger} c_{\kappa}$. We define operators connected with these as

$$(19) \quad \begin{aligned} L_{\kappa} &= a_{\kappa}^{\dagger} a_{\kappa} = a_{-\kappa} a_{\kappa}; \\ N_{\kappa} &= c_{\kappa}^{\dagger} c_{\kappa} = c_{-\kappa} c_{\kappa}; \end{aligned}$$

for $\kappa > 0$

From (15) and (19) we find easily,

$$(20) \quad \begin{aligned} L_{\kappa} &= \frac{1}{2} (N_{\kappa}^{(+)} + N_{\kappa}^{(-)}) + \frac{1}{2} (a_{\kappa}^{\dagger} \gamma_{\kappa} + \gamma_{\kappa}^{\dagger} a_{\kappa}), \\ N_{\kappa} &= \frac{1}{2} (N_{\kappa}^{(+)} + N_{\kappa}^{(-)}) - \frac{1}{2} (a_{\kappa}^{\dagger} \gamma_{\kappa} + \gamma_{\kappa}^{\dagger} a_{\kappa}), \end{aligned}$$

or

$$(21) \quad \begin{aligned} L_{\kappa} + N_{\kappa} &= N_{\kappa}^{(+)} + N_{\kappa}^{(-)}, \\ L_{\kappa} - N_{\kappa} &= a_{\kappa}^{\dagger} \gamma_{\kappa} + \gamma_{\kappa}^{\dagger} a_{\kappa}. \end{aligned}$$

From the representation (13) of the a_{κ} , γ_{κ} one sees that $L_{\kappa} - N_{\kappa}$ has no diagonal elements, or the expectation value

$$(22) \quad \bar{L}_{\kappa} - \bar{N}_{\kappa} = 0.$$

$N_{\kappa}^{(+)}$ and $N_{\kappa}^{(-)}$ are the numbers of neutrinos and anti-neutrinos in the state κ . We can assume that all states above a certain state are unoccupied,

$$i.e., \quad N_{\kappa}^{(+)} = 0 \quad \text{and} \quad N_{\kappa}^{(-)} = 0, \quad \text{for } \kappa > K.$$

Therefore

$$(23) \quad \sum_{\kappa} (L_{\kappa} + N_{\kappa}) \text{ is finite.}$$

From (22) it follows, that all eigenvalues of

$$(23) \quad \sum_{\kappa} (\bar{L}_{\kappa} - \bar{N}_{\kappa}) = \overline{\sum_{\kappa} (L_{\kappa} - N_{\kappa})}$$

are finite. Therefore

$$(24) \quad \sum_{\kappa} L_{\kappa} \quad \text{and} \quad \sum_{\kappa} N_{\kappa} \text{ are finite; } \quad \kappa > 0.$$

We shall make use of these results later.

With the help of the operators a_{κ} and c_{κ} we will presently define the important operator b_k first discovered by Jordan which obeys the Bose-Einstein commutation rules.

8. The Operator b_k .

Jordan has defined the operator b_k as

$$(25) \quad b_k = \frac{i}{\sqrt{|k|}} \sum_{\kappa=-\infty}^{\infty} a_{\kappa} c_{k-\kappa}$$

for $k = \pm 1, \pm 2, \pm 3, \dots$

We first observe that

$$(26) \quad b_k^\dagger = b_{-k}$$

for

$$\begin{aligned} b_k^\dagger &= -\frac{i}{\sqrt{|k|}} \sum_{\kappa} c_{k-\kappa}^\dagger a_{\kappa}^\dagger = \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{\kappa}^\dagger c_{k-\kappa}^\dagger \\ &= \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{-\kappa} c_{-k+\kappa} = \frac{i}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{\kappa} c_{-k-\kappa} = b_{-k} \end{aligned}$$

We will now obtain the commutation rules for b_k

$$\begin{aligned} [b_k, b_j] &= (b_k b_j - b_j b_k) = -\frac{1}{\sqrt{|k j|}} \sum_{\kappa, l} [a_{\kappa} c_{k-\kappa}, a_l c_{j-l}], \\ [a_{\kappa} c_{k-\kappa}, a_l c_{j-l}] &= a_{\kappa} [c_{k-\kappa}, a_l c_{j-l}] + [a_{\kappa}, a_l c_{j-l}] c_{k-\kappa} \\ &= -a_{\kappa} a_l [c_{k-\kappa}, c_{j-l}] + \{a_{\kappa}, a_l\} c_{j-l} c_{k-\kappa} \\ (27) \quad &= -a_{\kappa} a_l \delta_{k-\kappa, -j+l} + c_{j-l} c_{k-\kappa} \delta_{\kappa, -l}. \end{aligned}$$

Thus

$$(28) \quad [b_k, b_j] = \frac{1}{\sqrt{|k j|}} \sum_{-\infty}^{\infty} (a_{\kappa} a_{k+j-\kappa} - c_{j+\kappa} c_{k-\kappa}).$$

To evaluate the series we remember the result (24) that

$$(29) \quad \sum_{\kappa} I_{\kappa} = \sum_{\kappa} a_{-\kappa} a_{\kappa} \quad \text{and} \quad \sum_{\kappa} N_{\kappa} = \sum_{\kappa} c_{-\kappa} c_{\kappa}$$

are convergent. We further assume that the series

$$(30) \quad \sum_{\frac{1}{2}}^{\infty} a_{-\kappa+r} a_{\kappa} \quad \text{and} \quad \sum_{\frac{1}{2}}^{\infty} c_{-\kappa+r} c_{\kappa}$$

for any finite r , are convergent.*

Now we reorder the expression (28) in such a way that only terms of the form (30) appear:

$$\sqrt{|k j|} [b_k, b_j] = - \sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa} a_{\kappa} + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa} c_{j+\kappa} +$$

* This condition which has not been explicitly stated by Jordan, but which he really uses, seems to us to be indispensable.

$$\begin{aligned}
 & + \sum_{-\frac{1}{2}}^{-\infty} a_{\kappa} a_{k+j-\kappa} - \sum_{-\frac{1}{2}}^{\infty} c_{j+\kappa} c_{k-\kappa} \\
 & = - \sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa} a_{\kappa} + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa} c_{j+\kappa} + \sum_{\frac{1}{2}}^{\infty} a_{-\kappa} a_{k+j+\kappa} - \sum_{\frac{1}{2}}^{\infty} c_{j-\kappa} c_{k+\kappa}.
 \end{aligned}$$

Replacing in the third series $-\kappa$ by $k+j-\kappa$ and in the fourth series $-\kappa$ by $k-j-\kappa$, we get

$$\begin{aligned}
 \sqrt{|kj|} [b_k, b_j] & = - \sum_{\frac{1}{2}}^{\infty} a_{k+j-\kappa} a_{\kappa} + \sum_{\frac{1}{2}}^{\infty} c_{k-\kappa} c_{j+\kappa} \\
 (32) \quad & + \sum_{k+j+\frac{1}{2}}^{\infty} a_{k+j-\kappa} a_{\kappa} - \sum_{k-j+\frac{1}{2}}^{\infty} c_{k-\kappa} c_{j+\kappa}
 \end{aligned}$$

or

$$\begin{aligned}
 (33) \quad & = - \sum_{\frac{1}{2}}^{k+j-\frac{1}{2}} a_{k+j-\kappa} a_{\kappa} + \sum_{\frac{1}{2}}^{k-j-\frac{1}{2}} c_{k-\kappa} c_{j+\kappa} = \\
 & - \frac{1}{2} \sum_{\frac{1}{2}}^{k+j-\frac{1}{2}} (a_{k+j-\kappa} a_{\kappa} + a_{\kappa} a_{k+j-\kappa}) + \frac{1}{2} \sum_{\frac{1}{2}}^{k-j-\frac{1}{2}} (c_{k-\kappa} c_{j+\kappa} + c_{j+\kappa} c_{k-\kappa}).
 \end{aligned}$$

Thus using the commutation rules (18)

$$\sqrt{|kj|} [b_k, b_j] = 0, \quad \text{if } k+j \neq 0.$$

If $k+j=0$

$$\begin{aligned}
 k [b_k, b_{-k}] & = \frac{1}{2} \sum_{\frac{1}{2}}^{2k-\frac{1}{2}} (c_{k-\kappa} c_{-k+\kappa} + c_{-k+\kappa} c_{k-\kappa}) = \frac{1}{2} \cdot 2k \\
 (34) \quad & = k.
 \end{aligned}$$

Thus we get the commutation rules for b_k as

$$\begin{aligned}
 (35) \quad & b_k b_j - b_j b_k = 0, \quad \text{if } k+j \neq 0, \\
 & b_k b_{-k} - b_{-k} b_k = 1, \quad k > 0.
 \end{aligned}$$

9. Expression for b_k in Terms of a_{κ} and γ_{κ} .

If we substitute in the expression (25) for b_k , a_{κ} , γ_{κ} instead of a_{κ} , c_{κ} with the help of (15) we get

$$\begin{aligned}
 \sqrt{|k|} b_k & = \frac{1}{2} \sum_{-\infty}^{\infty} (a_{\kappa} + \gamma_{\kappa}) (a_{k-\kappa} - \gamma_{k-\kappa}) \\
 & = \frac{1}{2} \sum_{-\infty}^{\infty} (a_{\kappa} a_{k-\kappa} - \gamma_{\kappa} \gamma_{k-\kappa} - a_{\kappa} \gamma_{k-\kappa} + \gamma_{\kappa} a_{k-\kappa}).
 \end{aligned}$$

But

$$\sum_{-\infty}^{\infty} a_{\kappa} a_{k-\kappa} = \frac{1}{2} \sum_{-\infty}^{\infty} (a_{\kappa} a_{k-\kappa} + a_{k-\kappa} a_{\kappa}) = 0$$

$$\sum_{-\infty}^{\infty} \gamma_{\kappa} \gamma_{k-\kappa} = \frac{1}{2} \sum_{-\infty}^{\infty} (\gamma_{\kappa} \gamma_{k-\kappa} + \gamma_{k-\kappa} \gamma_{\kappa}) = 0$$

$$\text{and } \sum_{-\infty}^{\infty} \gamma_{\kappa} a_{k-\kappa} = - \sum_{-\infty}^{\infty} a_{k-\kappa} \gamma_{\kappa} = - \sum_{-\infty}^{\infty} a_{k+\kappa} \gamma_{-\kappa} = - \sum_{-\infty}^{\infty} a_{\kappa} \gamma_{k-\kappa}.$$

Thus we get

$$(36) \quad b_k = - \frac{1}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{\kappa} \gamma_{k-\kappa}$$

or

$$(37) \quad b_k = - \frac{1}{\sqrt{|k|}} \sum_{-\infty}^{\infty} a_{\kappa} a_{\kappa-k}^{\dagger}$$

A third expression given by Jordan is gained by splitting the above sum into terms with only positive indices :

$$(38) \quad b_k = - \frac{1}{\sqrt{|k|}} \left\{ \sum_{\kappa=1}^{k-1} a_{\kappa} \gamma_{k-\kappa} + \sum_{\kappa=1}^{\infty} (a_{k+\kappa} a_{\kappa}^{\dagger} - \gamma_{k+\kappa} \gamma_{\kappa}^{\dagger}) \right\}$$

10. The Operator B and its Commutation Properties with b_k

The operator B is defined by Kronig as

$$(39) \quad B = i \sum_{-\infty}^{\infty} a_l c_{-l}$$

and by Jordan as

$$(40) \quad \begin{aligned} B &= \sum_{\frac{1}{2}}^{\infty} (N_{\kappa}^{(+)} - N_{\kappa}^{(-)}) \\ &= \sum_{\frac{1}{2}}^{\infty} (a_{\kappa}^{\dagger} a_{\kappa} - \gamma_{\kappa}^{\dagger} \gamma_{\kappa}). \end{aligned}$$

The two definitions can be shown to be equivalent if we transform a 's and c 's to a 's and γ 's and by using the commutation rules. The first definition in (40) shows immediately (as pointed out by Jordan) that B has whole number eigenvalues 0, ± 1 , ± 2 ,

Kronig has shown that B commutes with all b_k defined in (25). We simply reproduce his proof.

$$Bb_k = - \frac{1}{\sqrt{|k|}} \sum_{l, m}^{\infty} a_l c_{-l} a_m c_{k-m},$$

$$\begin{aligned}
 Bb_k - b_k B &= \frac{1}{\sqrt{|k|}} \sum_{l, m}^{\infty} (a_m c_{k-m} a_l c_{-l} - a_l c_{-l} a_m c_{k-m}) \\
 (41) \qquad &= \frac{1}{\sqrt{|k|}} \sum_l^{\infty} (a_l a_{k-l} + c_{-l} c_{k+l}) = 0,
 \end{aligned}$$

using the commutation rules for a 's and c 's.

11. Photons

It is known that the photons in a Hohlraum can be represented by a set of variables b_k which satisfy commutation rules of the type (35). In the case of a one-dimensional Hohlraum the light wave could be represented by a wave function

$$(42) \qquad \psi(t - x/c) = \sum_{k=-\infty}^{\infty} b_k e^{2\pi i \nu_1 k(t-x/c)} = \phi^+.$$

In 3-dimensions there are some geometrical complications arising from the polarisation of light which do not affect the use of the variables* b_k but we do not treat these questions here

Before Jordan's work it was generally believed that there were two fundamental statistics, the Fermi-Dirac statistics and the Bose-Einstein statistics. The former is connected with wave functions anti-symmetric in the particles of the assembly, the latter with symmetric wave functions. *Jordan's mathematical results can be interpreted as the fundamental physical statement that the only primary statistics is the Fermi-Dirac one with anti-symmetric wave functions* If applied to processes in empty space, this leads to the idea that photons (as primary Bose-Einstein particles) do not exist at all, but that they are only a secondary effect appearing under special circumstances. The phenomena in empty space have really to be described by moving neutrinos and anti-neutrinos (or the corresponding waves). The phenomena attributed usually to photons are, according to Jordan, really simultaneous actions of pairs of neutrinos and anti-neutrinos. The exact formulation of these actions follows from the formulæ (25).

For a state with given numbers of neutrinos $N^{(+)}$ and $N^{(-)}$, the operator representing the *number of photons* in the k th state.

$$(43) \qquad P_k = b_k^+ b_k = b_{-k} b_k,$$

is in general not a diagonal matrix, *i.e.*, the number of photons has not definite values. But we can calculate its average or expectation value—the diagonal element of P_k :

$$\overline{P}_k (t_{1/2}, t_{-1/2}, t_{3/2}, t_{-3/2}, \dots, \dots)$$

* P. A. M. Dirac, *Quantum Mechanics*, 1935, p. 229

$$(44) = \sum_{t'_{1/2}, t'_{-1/2}, t'_{3/2}, t'_{-3/2}, \dots} | b_k (t'_{1/2}, t'_{-1/2}, t'_{3/2}, t'_{-3/2}, \dots; t_{1/2}, t_{-1/2}, t_{3/2}, t_{-3/2}, \dots) |^2.$$

We observe that each a_κ has only one non-vanishing element ± 1 , when t'_κ makes the jump $0 \rightarrow 1$ and when all the other t 's remain unchanged; a_{κ}^+ behaves in the same fashion except that the jump for t'_κ would be $1 \rightarrow 0$. The γ_κ behaves just in a similar way round as indicated in the scheme (14). Therefore $a_\kappa \gamma_{k-\kappa}$ for $\frac{1}{2} \leq \kappa \leq k - \frac{1}{2}$ has only one non-vanishing element ± 1 for $t_\kappa : 0 \rightarrow 1$ and $t_{k-\kappa} : 0 \rightarrow 1$.

One term of the first sum is consequently

$$N_{\kappa}^{(+)} N_{k-\kappa}^{(-)}.$$

In the same way the terms of the other sums are

$$N_{k+\kappa}^{(+)} (1 - N_{\kappa}^{(+)}) \text{ and } N_{k+\kappa}^{(-)} (1 - N_{\kappa}^{(-)}).$$

The result is

$$(45) \quad \bar{P}_k = \frac{1}{h} \sum_{\kappa = \frac{1}{2}}^{k - \frac{1}{2}} N_{\kappa}^{(+)} N_{k-\kappa}^{(-)} + \frac{1}{h} \sum_{\kappa = \frac{1}{2}}^{\infty} \{ N_{k+\kappa}^{(+)} (1 - N_{\kappa}^{(+)}) + N_{k+\kappa}^{(-)} (1 - N_{\kappa}^{(-)}) \}.$$

Jordan interprets this formula in the following way: There are two kinds of interaction of neutrinos and matter which are equivalent to an interaction of photons with matter

- (1) *Simultaneous absorption of a neutrino and an anti-neutrino whose total energy is equal to that of the energy change of the atom: $\kappa + (k - \kappa) = k$ (usually ascribed to the absorption of one photon).*
- (2) *Raman effect of neutrinos or anti-neutrinos. One neutrino (anti-neutrino) of the energy $k + \kappa$ is absorbed, another of the same kind of the energy κ is emitted*

The processes (1) and (2) are not essentially different, if we use the idea of only one kind of neutrinos having positive and negative energy states; the process (1) could be considered also as a Raman effect where a neutrino of positive energy is absorbed and one of negative energy is emitted. This is mathematically represented directly by the short formula (37)

12 Statistical Equilibrium.

The most important result of Jordan is the proof that this new conception of radiation leads to the correct results for the statistical equilibrium, i.e., Planck's law

We have two kinds of neutrinos satisfying the Fermi-Dirac statistics. The well-known formula for the entropy of an assembly of $N_{\nu}^{(+)}$ neutrinos and $N_{\nu}^{(-)}$ anti-neutrinos of nearly equal energy \bar{l} (in units $h\nu_1$) is

$$(46) \quad S = -k \sum_{\mu} \left\{ (1 - N_{\mu}^{(+)}) \log (1 - N_{\mu}^{(+)}) + N_{\mu}^{(+)} \log N_{\mu}^{(+)} \right\} + (1 - N_{\mu}^{(-)}) \log (1 - N_{\mu}^{(-)}) + N_{\mu}^{(-)} \log N_{\mu}^{(-)} \Big\}$$

k being the Boltzmann constant.

Since the anti-neutrinos correspond to holes in the multitude of neutrinos with negative energy, a neutrino can disappear only by falling in a hole, or by a simultaneous disappearance of an anti-neutrino. Therefore

$$(47) \quad \sum_{\mu} (N_{\mu}^{(+)} - N_{\mu}^{(-)}) = B,$$

is constant Besides we have the total energy given as

$$(48) \quad \sum_{\mu} \mu (N_{\mu}^{(+)} + N_{\mu}^{(-)}) = \frac{E_l}{h\nu_1}.$$

Using two multipliers which we call $\psi\beta$ and β , we get by the variation of S given by (46) under the two conditions (47) and (48)

$$\log \frac{1 - N_{\mu}^{(+)}}{N_{\mu}^{(+)}} = \beta (l + \psi),$$

$$\log \frac{1 - N_{\mu}^{(-)}}{N_{\mu}^{(-)}} = \beta (l - \psi).$$

From this we find the Fermi distribution law

$$(49) \quad N_{\mu}^{(+)} = \frac{1}{e^{\beta(l+\psi)} + 1}, \quad N_{\mu}^{(-)} = \frac{1}{e^{\beta(l-\psi)} + 1}$$

or if we introduce the notations

$$y = e^{-\beta l} \quad \text{and} \quad a = e^{-\beta \psi},$$

$$(50) \quad N_{\mu}^{(+)} = \frac{a y}{1 + a y} \quad \text{and} \quad N_{\mu}^{(-)} = \frac{\frac{y}{a}}{1 + \frac{y}{a}}.$$

Introducing these into the expression of the entropy and applying the second law of thermodynamics it is shown in the well-known manner that $\beta = h\nu_1/kT$. We substitute these expressions (50) in Jordan's formula (45),

$$\overline{P_l} = \frac{1}{l} \sum_{\kappa=\frac{1}{2}}^{l-\frac{1}{2}} N_{\kappa}^{(+)} N_{l-\kappa}^{(-)} + \frac{1}{l} \sum_{\kappa=\frac{1}{2}}^{\infty} \{N_{l+\kappa}^{(+)} (1 - N_{\kappa}^{(+)}) + N_{l+\kappa}^{(-)} (1 - N_{\kappa}^{(-)})\}.$$

Denoting

$$\frac{\kappa}{l} = \omega,$$

we have

$$e^{-\beta \kappa} = y \omega$$

and $d\kappa = l d\omega$, $\nu_1 l = \nu$.

We replace the sum by integrals* and get

$$(51) \quad P(\nu) = \int_0^1 \frac{ay\omega}{1+ay\omega} \cdot \frac{\frac{1}{a}y^{1-\omega}}{1+\frac{1}{a}y^{1-\omega}} d\omega + \int_0^\infty \left\{ \frac{ay^{1+\omega}}{1+ay^{1+\omega}} \cdot \frac{1}{1+ay\omega} \right. \\ \left. + \frac{\frac{1}{a}y^{1+\omega}}{1+\frac{1}{a}y^{1+\omega}} \cdot \frac{1}{1+\frac{1}{a}y\omega} \right\} d\omega.$$

The first we write

$$\int_0^1 \frac{y d\omega}{(1+ay\omega)(1+\frac{1}{a}y^{1-\omega})} = \int_0^\infty - \int_1^\infty,$$

which by changing in the second integral ω to $1+\omega$ becomes

$$y \int_0^\infty \left\{ \frac{1}{(1+ay\omega)(1+\frac{1}{a}y^{1-\omega})} - \frac{1}{(1+ay^{1+\omega})(1+\frac{1}{a}y^{-\omega})} \right\} d\omega.$$

The second integral here cancels the first part of the remaining integral in (51) so that

$$P(\nu) = y \int_0^\infty \left\{ \frac{1}{(1+ay\omega)(1+\frac{1}{a}y^{1-\omega})} + \frac{\frac{1}{a}y^{1+\omega}}{(1+\frac{1}{a}y^{1+\omega})(1+\frac{1}{a}y\omega)} \right\} d\omega \\ = y \int_0^\infty \left\{ \frac{ay\omega^{-1}}{(1+ay\omega)(1+ay\omega^{-1})} + \frac{ay^{-\omega-1}}{(1+ay^{-\omega})(1+ay^{-\omega-1})} \right\} d\omega \\ = \int_{-\infty}^\infty \frac{ay\omega}{(1+ay\omega)(1+ay\omega^{-1})} d\omega.$$

We write the above formula as

$$(52) \quad \bar{P}(\nu) = \int_{-\infty}^\infty \frac{ay\omega}{1+ay\omega} \left(1 - \frac{ay\omega^{-1}}{1+ay\omega^{-1}} \right) d\omega$$

$$(53) \quad = \boxed{\frac{1}{i} \sum_{\kappa=-\infty}^{\infty} N_{\kappa} (1 - N_{\kappa-i})}$$

* One can also readily evaluate these integrals by substituting $\frac{1-z}{z}$ for $ay\omega$ in the first integral and $\frac{1-z}{z}$ for $ay^{1+\omega}$ and $\frac{1-z}{z}$ for $\frac{1}{a}y^{1-\omega}$ in the other integrals.

We can interpret this formula by assuming only one kind of neutrinos with the number N_κ in the state κ where κ may be positive or negative. Then the formula gives the average photon density of energy l as a Raman effect with the universal rule: absorption of a neutrino of any (positive or negative) energy κ and simultaneous emission of a neutrino with the energy $\kappa - l$. We mention this to confirm our idea that the introduction of a spin of the neutrino by Jordan is quite unnecessary.

Since $y < 1$ we can substitute

$$ay\omega = \frac{1-z}{z},$$

$$\text{so that } ay\omega \, d\omega = -\frac{1}{z^2 \log y} dz.$$

Then

$$\begin{aligned} \overline{P(\nu)} &= - \int_0^1 \frac{1}{\log y} \cdot \frac{dz}{z^2 \left(1 + \frac{1-z}{z}\right) \left(1 + \frac{1}{y} \frac{1-z}{z}\right)} = - \frac{y}{\log y} \int_0^1 \frac{dz}{1 + (y-1)z} \\ &= - \frac{y}{\log y} \left[\frac{\log(1 + (y-1)z)}{y-1} \right]_0^1 = \frac{y}{1-y}. \end{aligned}$$

Introducing here the value of y , we get

$$(54) \quad \overline{P(\nu)} = \frac{e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} = \frac{1}{e^{\frac{h\nu}{kT}} - 1}.$$

This is the well-known expression for the photon density which by multiplication with the number of photons in the interval $d\nu$ leads to Planck's formula of radiation.

13. Relation between the Energy of Neutrinos and Photons

We have already remarked that a neutrino field with definite numbers of neutrinos of both kinds, $N_{\kappa^{(+)}}$, $N_{\kappa^{(-)}}$ is in general not equivalent to a photon field of a given number of photons, P_k . In the language of quantum mechanics we can understand this in the following way. There is a Hilbert space representing all the states of the field. If we choose a co-ordinate system in which the quantities $N_{\kappa^{(+)}}$, $N_{\kappa^{(-)}}$ are all represented by diagonal matrices, the quantities P_k are not so. But there will be another co-ordinate system where P_k 's are diagonal; we will then have a pure photon state. The question is to form an idea as to the relation of these different states.

For this purpose we prove an identity derived first by de Kronig connecting the total energy of the neutrinos with that of the photons. The energy of the neutrinos is

$$(55) \quad E = \sum_{n=\frac{1}{2}}^{\infty} n (L_n + N_n) = \sum_{n=\frac{1}{2}}^{\infty} n (N_n^{(+)} + N_n^{(-)}).$$

The energy of the photons is

$$(56) \quad W = \sum_{n=1}^{\infty} n P_n$$

The proposition is

$$(57) \quad \boxed{E - W = \frac{1}{2} B^2},$$

where B is the quantity defined in (39) which, as we have shown, commutes with all the b_k . Kronig's proof of the proposition is as follows.

$$\begin{aligned} W &= \sum_1^{\infty} k P_k = \sum_1^{\infty} k b_k^{\dagger} b_k \\ &= - \sum_{l,m=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l c_{-k-l} a_m c_{k-m} \\ (58) \quad &= \sum'_{l,m=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l a_m c_{-k-l} c_{k-m} + \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l a_{-l} c_{-k-l} c_{k+l}, \end{aligned}$$

where the dash over the summation sign indicates that $l \neq -m$.

Changing k to $-k$, l to m , m to l in the first part of (58) and using the commutation laws, we get

$$(59) \quad W = \sum'_{l,m=-\infty}^{\infty} \sum_{k=-1}^{-\infty} a_l a_m c_{-k-l} c_{k-m} + \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} a_l a_{-l} c_{-k-l} c_{k+l}.$$

From (39) we see that

$$(60) \quad B^2 = \sum'_{l,m=-\infty}^{\infty} a_l a_m c_{-l} c_{-m} + \sum_{l=-\infty}^{\infty} a_l a_{-l} c_{-l} c_l.$$

We first observe that

$$(61) \quad \sum'_{l,m=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} a_l a_m c_{-k-l} c_{k-m} = \sum'_{l,m=-\infty}^{\infty} a_l a_m \sum_{k=-\infty}^{\infty} c_{-k-l} c_{k-m} = 0,$$

using the commutation rules for c 's. Thus adding (58), (59) and (60) and using (61), we get

$$2W + B^2 = 2 \sum_{l=-\infty}^{\infty} a_l a_{-l} \sum_{k=1}^{\infty} c_{-k-l} c_{k+l} + \sum_{l=-\infty}^{\infty} a_l a_{-l} c_{-l} c_l.$$

We split the summations in a manner such that each summation index so that k or l assumes only positive values.

$$\begin{aligned}
 2W + B^2 &= 2 \sum_{l=\frac{1}{2}}^{\infty} a_l a_{-l} \sum_{k=1}^{\infty} c_{-k-l} c_{k+l} + 2 \sum_{l=\frac{3}{2}}^{\infty} a_{-l} a_l \sum_{k=1}^{l-\frac{1}{2}} c_{-k+l} c_{k-l} \\
 &+ 2 \sum_{l=\frac{3}{2}}^{\infty} a_{-l} a_l \sum_{k=l+\frac{1}{2}}^{\infty} c_{-k+l} c_{k-l} + 2 a_{-\frac{1}{2}} a_{\frac{1}{2}} \sum_1^{\infty} c_{-k+\frac{1}{2}} c_{k-\frac{1}{2}} \\
 &+ \sum_{l=\frac{1}{2}}^{\infty} a_l a_{-l} c_{-l} c_l + \sum_{l=\frac{1}{2}}^{\infty} a_{-l} a_l c_l c_{-l} \\
 &= 2 \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) \sum_{k=1}^{\infty} N_{k+l} + \sum_{l=\frac{3}{2}}^{\infty} L_l \sum_{k=1}^{l-\frac{1}{2}} (1 - N_{-k+l}) \\
 &+ 2 \sum_{l=\frac{3}{2}}^{\infty} L_l \sum_{k=l+\frac{1}{2}}^{\infty} N_{k-l} + 2 L_{\frac{1}{2}} \sum_{k=1}^{\infty} N_{k-\frac{1}{2}} \\
 &+ \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) N_l + \sum_{l=\frac{1}{2}}^{\infty} L_l (1 - N_l) \\
 &= 2 \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) \sum_{j=l+1}^{\infty} N_j + 2 \sum_{l=\frac{3}{2}}^{\infty} L_l \sum_{j=\frac{1}{2}}^{l-1} (1 - N_j) \\
 &\quad + 2 \sum_{l=\frac{3}{2}}^{\infty} L_l \sum_{k=\frac{1}{2}}^{\infty} N_j \\
 &+ 2 L_{\frac{1}{2}} \sum_{k=1}^{\infty} N_{k-\frac{1}{2}} + \sum_{l=\frac{1}{2}}^{\infty} (1 - L_l) N_l + \sum_{l=\frac{1}{2}}^{\infty} L_l (1 - N_l) \\
 &= (L_{\frac{1}{2}} + N_{\frac{1}{2}}) + 2 \sum_{l=\frac{3}{2}}^{\infty} \sum_{j=l+1}^{\infty} N_j + 2 \sum_{l=\frac{3}{2}}^{\infty} L_l \sum_{j=\frac{1}{2}}^{l-1} 1 \\
 &\quad + 3 \sum_{\frac{3}{2}}^{\infty} N_j + \sum_{\frac{3}{2}}^{\infty} L_j \\
 &= (L_{\frac{1}{2}} + N_{\frac{1}{2}}) + 2 \sum_{\frac{3}{2}}^{\infty} (l - \frac{3}{2}) N_l + 2 \sum_{\frac{3}{2}}^{\infty} (l - \frac{1}{2}) L_l + 3 \sum_{\frac{3}{2}}^{\infty} N_l + \sum_{\frac{3}{2}}^{\infty} L_l \\
 &= 2 \sum_{l=\frac{1}{2}}^{\infty} l (L_l + N_l) = 2E.
 \end{aligned}$$

Thus

$$(62) \quad 2W + B^2 = 2E$$

or

$$\boxed{E - W = B^2/2}$$

Now we can answer the question put forward in the beginning of this section.

The necessary and sufficient condition that the whole neutrino energy appears in the form of photon energy is $B = 0$ or $N^{(+)} = N^{(-)}$. These states are called pure photon states or pure light fields.

The other extreme case is a pure neutrino field if $W = 0$ and $E = B^2/2$.

There are innumerable cases intermediate between these pure fields. As we have shown in (41) that B commutes with all b_k , the matrices representing b_k are reducible; they split up into finite parts corresponding to the eigenvalues $0, \pm 1, \pm 2, \dots$, of B . For, we can take a matrix representation where B is diagonal, if r and s symbolise states of the neutrinos, then

$$B(r, s) = B(r) \delta(r, s).$$

The commutability

$$B b_k = b_k B$$

gives in this representation

$$B(r) \delta(r, t) b_k(t, s) = b_k(r, t) B(t) \delta(t, s),$$

$$\text{or} \quad B(r) b_k(r, s) = b_k(r, s) B(s),$$

from which we conclude that $b_k(r, s) = 0$ for each pair of states which do not belong to the same eigenvalue of B , $B(r) \neq B(s)$. Therefore all impure fields can be classified with 0 , or 1 , or $2, \dots$ not compensated neutrinos (or anti-neutrinos); Jordan calls this number the *resultant neutrino charge*.

14. Conclusion.

The standpoint assumed by Jordan is the following. Before the radio-active processes revealed the probability of the existence of the neutrinos, the only experimentally known wave fields were those which appear now as pure light fields. They turn out to be only a limiting case of a very much larger multitude of possible fields, which contain free (not compensated) neutrinos. The validity of this hypothesis could be experimentally tested by a study of a possible influence of radiation fields on the β -decay. If it is true that the β -emission is accompanied by an emission of a neutrino there should be an influence of an external neutrino field on the β -emission. But since light fields are nothing than neutrino fields (with neutrino pairs) we should also expect an influence of light radiation on the β -decay. The law of this interaction has yet to be calculated.

We wish to make another remark. Quantum mechanics was started by replacing the Fourier amplitudes $q_k e^{2\pi i \nu_0 k t}$ of co-ordinate function $q(t)$ by matrix elements with two indices $q_{kl} e^{2\pi i \nu_{kl} t}$. In analogy, one could expect that in a quantum field theory the Fourier elements $q_k e^{2\pi i \nu_0 k(t-x/c)}$ of a quantity representing a progressive wave $q(t-x/c)$ should be replaced by matrix elements $q_{kl} e^{2\pi i \nu_{kl}(t-x/c)}$. Here, as in quantum

mechanics, one should expect the combination law $\nu_{kl} + \nu_{lm} = \nu_{km}$. In the previous theories of radiation fields, there was no indication that something like that would lead to a deeper understanding. But here, in Jordan's neutrino theory, we have for the photon amplitudes the expression

$$(63) \quad \frac{\sqrt{|k|}}{i} b_k = \sum_{l=-\infty}^{\infty} a_l c_{k-l},$$

where the right-hand sum is apparently the coefficient of the two Fourier series with the coefficients a_k, c_k . Now it suggests itself that we have really to do with matrices and their multiplication: a_{kl}, c_{kl} and

$$(64) \quad \boxed{\sum_{n=-\infty}^{\infty} a_{kn} c_{nl}}$$

where each element of these matrices is again a matrix or more generally a non-commuting quantity of the kind treated here. It seems to be attractive to follow this indication.

During writing this article, we have received the manuscript of a new article* of Jordan and de Kronig in which they treat the 3-dimensional case. There appear no new fundamental difficulties, but there are some interesting features which are beyond the scope of this article to be reported. Also in this paper, Jordan and Kronig have not changed their standpoint to consider the distinction between the neutrino and the anti-neutrino as the value of the spin instead of states and holes as we do here.

* We are very grateful for having had the privilege of knowing about this work before publication.

ON THE ERROR TERM IN A CERTAIN SUM.

BY M. L. N. SARMA, B A. (HONS.)

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(Communicated by Dr. S. Chowla.)

Let $\phi(n)$ denote the number of positive integers not exceeding n and prime to it. It is known that if

$$\sum_{n=1}^x \phi(n) - \frac{3}{\pi^2} x^2 = E(x),$$

then¹

$$(1) \quad E(x) = O(x \log x),$$

$$(2) \quad E(x) = \Omega(x \log \log \log x),$$

$$(3) \quad \sum_{r=1}^R E(x) \sim \frac{3}{2\pi^2} R^2.$$

The object of this note is to refute the conjecture that

(?) $E(1), E(2), E(3), \text{ etc.},$ are all positive. In fact calculation shows that the least integral value of m for which $E(m) < 0$ is $m = 820$.

The following is a table of values of $\sum_{n=1}^x \phi(n)$ and of $E(x)$ for different values of x . We write

$$\Phi(x) = \sum_{n=1}^x \phi(n).$$

x	$\Phi(x)$	$E(x)$
300	27398	41.27
350	37330	94.45
400	48678	43.81
450	61634	81.35
500	76116	125.08
550	92022	72.98
600	109500	73.07
650	128602	177.34
700	149018	75.79
750	171018	38.43
800	194750	213.24
820	204376	-9.18

For $821 \leq m$ (integral) ≤ 1000 we find that $E(m)$ is positive again.

¹ For (1) see Landau's "Handbuch der Primzahlen II". (2), (3) and the conjecture (?) are due to Chowla and Pillai. See Journ. London Math. Soc., 1930, 5, 95-101.

PILLAI'S EXACT FORMULA FOR THE NUMBER $g(n)$ IN WARING'S PROBLEM.

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§1. Let $g(n; \beta_1, \beta_2)$ denote the number

$$\text{Max}_{\beta_1 \leq m \leq \beta_2} g(n, m)$$

where $g(n, m)$ is the least value of s such that m can be expressed as a sum of s n th. powers ≥ 0 . Thus $g(n; 1, \infty) = g(n)$.

Let $3^n = l \cdot 2^n + r$ ($0 < r < 2^n$), so that r depends only on n . Pillai has shown that¹

Theorem 1 If $n > n_0$, and

$$(1) \left(\frac{1}{3}\right)^n + 2 \left(\frac{1}{4}\right)^n \leq r \leq 2^n - \left(\frac{3}{2}\right)^n - \left(\frac{1}{3}\right)^n - 2\left(\frac{5}{4}\right)^n,$$

$$\text{then } g(n; 1, \beta) = 2^n + l - 2$$

$$\text{where } \beta = n^{5n^{11}}.$$

This is his lemma 15, and a slightly modified proof has been published by Padhy.² Pillai proceeds to prove by the Vinogradow method (*Annals of Mathematics*, May 1935) that

Theorem 2. If $n > n_0$ then

$$g(n; \beta, \infty) \leq 2n^9,$$

$$\text{where } \beta = n^{5n^{11}}.$$

It is an immediate consequence of these two theorems that

Theorem 3. If r satisfies (1) above, then, for $n > n_0$,

$$g(n) = 2^n + l - 2.$$

In this note we prove that

Theorem 4. (1) is true for infinitely many n .

This is obviously a consequence of

Theorem 5. Let $f(n)$ denote the fractional part of $(\frac{2}{3})^n$. Then the inequality

$$\frac{1}{3} \leq f(n) \leq \frac{2}{3}$$

is true for infinitely many n .

From theorems 4 (or 5) and 3 we obtain

Theorem 6 Pillai's exact formula for $g(n)$, namely

$$g(n) = 2^n + l - 2.$$

¹ *Annamalai University Journal*, March 1936, 5, No. 2.

² See the paper which follows this.

is true for infinitely many n .

§2. Write $(\frac{3}{2})^n = l_n + f(n)$, so that l_n is an integer.

Lemma 1. If $0 < f(m) < \frac{1}{8}$, then, either

$$(i) \frac{1}{8} \leq f(m+1) \leq \frac{3}{4}$$

$$\text{or } (ii) f(m+1) = \frac{3}{2} f(m), f(m+1) < \frac{1}{8}.$$

Proof.—We have

$$(\frac{3}{2})^m = l_m + f(m), 0 < f(m) < \frac{1}{8}.$$

If $l_m \equiv 1 \pmod{2}$ it follows that

$$\frac{1}{8} < f(m+1) = \frac{1}{2} + \frac{3}{2} f(m) < \frac{3}{4},$$

and thus (i) holds.

If, however, $l_m \equiv 0 \pmod{2}$, we obtain

$$(2) f(m+1) = \frac{3}{2} f(m) \leq \frac{1}{8} \cdot \frac{3}{2} = \frac{1}{4}$$

From (2), either

$$(a) f(m+1) = \frac{3}{2} f(m) \text{ and } \frac{1}{8} \leq f(m+1) \leq \frac{1}{4}$$

or

$$(\beta) f(m+1) = \frac{3}{2} f(m) \text{ and } f(m+1) < \frac{1}{8}.$$

In case (a), (i) holds. Case (β) is (ii). Hence the lemma

Repeated application of lemma 1 gives the generalized

Lemma 2. If $f(m+r) < \frac{1}{8}$ [$r = 0, 1, 2, \dots, s-1$]

then, either,

$$(i) \frac{1}{8} \leq f(m+s) \leq \frac{3}{4}$$

or

$$(ii) f(m+s) = (\frac{3}{2})^s f(m), f(m+s) < \frac{1}{8}.$$

An exactly similar reasoning proves that—writing $\theta(m)$ for $1 - f(m)$,

Lemma 3. Lemma 2 is true when $f(m)$ is replaced by $\theta(m)$ throughout.

Since $f(m)$ is fixed, and $(\frac{3}{2})^s \rightarrow \infty$ as $s \rightarrow \infty$, (ii) of lemma 2 will be false for a certain s , and hence

Lemma 4. If $0 \leq f(m) < \frac{1}{8}$, then there exists an integer $s = s(m)$ such that

$$\frac{1}{8} \leq f(m+s) \leq \frac{3}{4}. \quad [s > 0].$$

Similarly from lemma 3 we get lemma 4 with the function $f(m)$ replaced by $\theta(m)$, which means that, since $\theta(m) = 1 - f(m)$,

Lemma 5. If $f(m) > \frac{5}{8}$, then there exists an integer $s = s(m)$ such that

$$\frac{1}{4} \leq f(m+s) \leq \frac{5}{8}. \quad [s > 0].$$

From lemmas 4 and 5, theorem 4 is an immediate consequence.

§3. S. S. Pillai has communicated to me the more difficult result that the number of solutions of

$$f(n) \leq 1 - \frac{l+3}{2^n}, 1 \leq n \leq x$$

is greater than $\frac{x}{4}$ for large x . But this result does not contain theorem 5.

PILLAI'S EXACT FORMULA FOR THE NUMBER $g(n)$ IN WARING'S PROBLEM.

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1. Introduction

LET $g(n, \beta)$ denote the least value s required to represent every positive integer $\leq \beta$ as a sum of s non-negative n th powers. Further let $l = [(\frac{2}{3})^n]$, where $[x]$ denotes the integral part of x . Let $3^n = l2^n + r$, so that r depends only on n . S. S. Pillai has proved¹

Theorem 1. If $r \leq 2^n - (l + 3)$, $\beta = n^{5n+1}$, then

$$g(n, \beta) = 2^n + l - 2$$

for $n > n_0$.

From this he deduces by Vinogradov's method a formula for $g(n) \{= g(n, \infty)\}$ which is exact in most cases². On account of the importance of Pillai's formula for $g(n)$ it was thought worthwhile to give a slightly simplified and more complete³ account of the proof of Theorem 1. For the sake of simplicity I confine myself to smaller range of values of r and prove, in fact,

Theorem 2. If $(\frac{4}{3})^n + 2(\frac{5}{4})^n \leq r \leq 2^n - (\frac{3}{2})^n - (\frac{4}{3})^n - 2(\frac{5}{4})^n$, then

$$g(n, n^A) = 2^n + l - 2,$$

where A is any preassigned (arbitrarily large but fixed) number, and $n > n_0(A)$.

2 Lemmas.

In this section I give an account of Pillai's lemmas. Let $\nu = \frac{1}{n}$. An n th power must be understood to mean the n th power of an integer ≥ 0 .

*Lemma 1.*⁴ If every integer M for which $f < M \leq h$ is a sum of $(s-1)$, n th powers, and if m is the highest integer such that

$$(m+1)^n - m^n < h - f,$$

¹ "On Waring's Problem," *Annamalai University Journal*, 5, No. 2. Theorem 1 is proved in lemmas 12 to 18. My thanks are due to Dr. Chowla for putting me into touch with Pillai's work.

² See the preceding note by S. Chowla.

³ Pillai's proofs of certain lemmas, especially those of lemmas 16 and 17, are incomplete.

⁴ This lemma is due to L. E. Dickson. The proof given here is mine own.

then every integer in the interval $[f, h + (m + 1)^n]$ is a sum of s , n th powers.

Proof. It is necessary to prove the lemma only for the interval $[h, h + (m + 1)^n]$. For the numbers M of this interval, we have

$$h - (m + 1)^n < M - (m + 1)^n \leq h$$

Now every M such that

$$\begin{aligned} f < M - (m + 1)^n &\leq h \\ \text{i.e., } f + (m + 1)^n < M &\leq h + (m + 1)^n \end{aligned}$$

is a sum of $(s - 1 + 1 =) s$, n th powers. So it is sufficient to prove the lemma for the interval $[h, f + (m + 1)^n]$ or for the interval $[h, h + m^n]$, since $f + (m + 1)^n < h + m^n$. Since

$$(r + 1)^n - r^n < h - f, \quad \text{for } r < m,$$

we can repeat this process (that of lessening the interval) m times and conclude at the end that the lemma is true if it is true for the interval $[h, h + 1]$. Since $(h + 1)$ is a sum of $(s - 1 + 1 =) s$, n th powers, the lemma is proved.

Lemma 2. If m is any positive integer ≥ 2 , then any integer N is expressible in the form

$$N = M + a,$$

where M is a sum of $\frac{2 \log N}{\log 2} \left(\frac{m}{m-1} \right)^n$, n th powers and $0 \leq a < m^n$.

Proof (1) Let $N < 2 m^n$. Then $N = b m^n + a$, where $b \leq 1$ and $0 \leq a < m^n$.

$$\text{Obviously } b \leq \frac{2 \log N}{\log 2} \left(\frac{m}{m-1} \right)^n, \quad (\text{since if } b = 1, N > m^n).$$

(2) Let $N > 2 m^n$. Put $r_0 = N$.

Let $b_1 = \left[\left(\frac{r_0}{2} \right)^n \right]$, $r_0 = q_1 b_1^n + r_1$, where $q_1 = \left[\left(\frac{r_0}{b_1^n} \right) \right]$, $r_1 < b_1^n$. Then $r_1 \leq \frac{r_0}{2}$.

Put $b_2 = \left[\left(\frac{r_1}{2} \right)^n \right]$, $r_1 = q_2 b_2^n + r_2$, where $q_2 = \left[\left(\frac{r_1}{b_2^n} \right) \right]$, $r_2 < b_2^n$.

$$\text{So } r_2 \leq \frac{r_1}{2} \leq \frac{r_0}{2^2}.$$

Put $b_3 = \left[\left(\frac{r_2}{2} \right)^n \right]$ and so on.

Then $N = r_0 = q_1 b_1^n + \dots + q_l b_l^n + r_l$, where $r_l \leq \frac{r_0}{2^l} = \frac{N}{2^l}$,

$$b_l = \left[\left(\frac{r_{l-1}}{2} \right)^n \right], \quad q_l = \left[\left(\frac{r_{l-1}}{b_l^n} \right) \right].$$

Since $r_0 \geq 2m^n$, it is possible to choose l so that

$$r_{l-1} \geq 2m^n > r_l$$

Put $r_l = bm^n + a$, where $b \leq 1$ and $0 \leq a < m^n$.

So $N = M + a$,

where M is a sum of $(q_1 + \dots + q_l + b)$, n th powers and $0 \leq a < m^n$.

Now for $k = 1, 2, \dots, l$

$$\begin{aligned} q_k &\leq \frac{r_{k-1}}{b_k^n} = \frac{r_{k-1}}{\left[\left(\frac{r_{k-1}}{2}\right)^n\right]} \leq \frac{r_{k-1}}{\left\{\left(\frac{r_{k-1}}{2}\right)^n - 1\right\}} \\ &= \frac{2}{\left\{1 - \left(\frac{2}{r_{k-1}}\right)^n\right\}} \leq \frac{2}{\left\{1 - \left(\frac{2}{r_{l-1}}\right)^n\right\}} \end{aligned}$$

since the r 's form a decreasing sequence,

$$\leq \frac{2}{\left\{1 - \left(\frac{2}{2m^n}\right)^n\right\}} = 2 \left(\frac{m}{m-1}\right)^n.$$

Also $b \leq 1 < 2 \left(\frac{m}{m-1}\right)^n.$

Hence $q_1 + \dots + q_l + b \leq 2(l+1) \left(\frac{m}{m-1}\right)^n.$

Moreover

$$\frac{N}{2^{l-1}} \geq r_{l-1} \geq 2m^n, \text{ i.e., } \frac{2N}{m^n} \geq 2^{l+1}$$

Since $m \geq 2$ we have $N \geq 2^{l+1}$, i.e., $l+1 \leq \frac{\log N}{\log 2}.$

Thus the lemma is proved.

Lemma 3. If every positive integer M such that $F < M \leq F + 2^n$ is the sum of s , n th powers, then every positive integer in the interval (F, n^n) is the sum of

$$s + \left(\frac{3}{2}\right)^n + \left(\frac{4}{3}\right)^n + 2\left(\frac{5}{4}\right)^n - 3,$$

n th powers, provided $n > n_0(A).$

Proof. For the interval $[F, F + 2^n]$, the m of lemma 1 is unity. So every integer in the interval $[F, F + 2 \cdot 2^n]$ is a sum of $(s+1)$, n th powers. In this way we see that every integer in the interval $[F, F + 3^n]$ is a sum of $s + \left(\frac{3}{2}\right)^n$, n th powers. In fact, the same argument shows that every positive integer in the interval $[F, F + m^n]$ is a sum of

$$s + \left(\frac{3}{2}\right)^n + \left(\frac{4}{3}\right)^n + \dots + \left(\frac{m}{m-1}\right)^n$$

n th powers.

Now let $F < N \leq n^A$. By lemma 2

$$N - F - 1 = M + a,$$

where M is a sum of $\frac{2 \log (N - F - 1)}{\log 2} \left(\frac{m}{m-1}\right)^n$

n th powers and $0 \leq a < m^n$.

Hence $N = M + (a + F + 1)$, and $F < (a + F + 1) \leq F + m^n$.

So $(a + F + 1)$ is a sum of

$$s + \left(\frac{3}{2}\right)^n + \dots + \left(\frac{m}{m-1}\right)^n,$$

n th powers. Hence N is a sum of

$$s + \left(\frac{3}{2}\right)^n + \dots + \left(\frac{m}{m-1}\right)^n + 2 \frac{\log (N - F - 1)}{\log 2} \left(\frac{m}{m-1}\right)^n,$$

n th powers.

Since $(N - F - 1) < n^A$,

$$\left(\frac{3}{2}\right)^n + \dots + \left(\frac{m}{m-1}\right)^n + 2 \frac{\log (N - F - 1)}{\log 2} \left(\frac{m}{m-1}\right)^n < \left(\frac{3}{2}\right)^n - 3,$$

when $m = 7$ and $n > n_0$ (A)

Hence the lemma follows.

3. Proof of Theorem 2.

(1) Every positive integer $< l2^n$ is of the form $a2^n + b$, where $a < l$, $b < 2^n$, and so is a sum of $l - 1 + 2^n - 1$, n th powers. Hence every positive integer $\leq l2^n$ is a sum of $2^n + l - 2$, n th powers.

(2) Every integer x in $l2^n \leq x < 3^n$ is of the form $l2^n + f$, where $f < r$, and so is a sum of $l + r - 1$, n th powers.

(3) Every integer y in $3^n \leq y < (l + 1)2^n$ is of the form $3^n + \theta$, where $\theta < 2^n - r$, and so is a sum of $1 + 2^n - r - 1$, n th powers.

(4) $(l + 1)2^n$ is a sum of $l + 1$, n th powers.

$$\text{Now } l + r - 1 \leq \left(\frac{3}{2}\right)^n + 2^n - \left(\frac{3}{2}\right)^n - \left(\frac{3}{2}\right)^n - 2 \left(\frac{3}{4}\right)^n - 1 < 2^n - \left(\frac{3}{2}\right)^n - 2 \left(\frac{3}{4}\right)^n,$$

$$2^n - r < 2^n - \left(\frac{3}{2}\right)^n - 2 \left(\frac{3}{4}\right)^n;$$

and $l + 1 \leq \left(\frac{3}{2}\right)^n + 1 < 2^n - \left(\frac{3}{2}\right)^n - 2 \left(\frac{3}{4}\right)^n$, for the given range of values of r .

Hence from (2), (3) and (4), every integer in the interval $[l2^n, (l + 1)2^n]$ is a sum of

$$2^n - \left(\frac{3}{2}\right)^n - 2 \left(\frac{3}{4}\right)^n$$

n th powers. Hence, by lemma 3, every integer in the interval $[l2^n, n^A]$ is a sum of

$$2^n + \left(\frac{3}{2}\right)^n - 3 \leq 2^n + l - 2$$

n th powers.

From (1) and above we notice that every integer $\leq n^{\wedge}$ is a sum of $2^n + l - 2$, n th powers. The number $l2^n - 1$ requires exactly $2^n + l - 2$, n th powers. Hence

$$g(n, n^{\wedge}) = 2^n + l - 2$$

for $n > n_0$ (A).

Pillai proceeds to show by Vinogradov's method that every integer $\geq \beta = n^{5n^{11}}$ needs at most $2n^9$, n th powers for $n > n_0$. Hence by Theorem 2 every integer needs

$$\text{Max } (2 + l - 2, 2n^9) = 2^n + l - 2$$

n th powers for $n > n_0$ and

$$\left(\frac{4}{3}\right)^n + 2\left(\frac{5}{4}\right)^n \leq r \leq 2^n - \left(\frac{3}{2}\right)^n - \left(\frac{4}{3}\right)^n - 2\left(\frac{5}{4}\right)^n.$$

ON THE BAND SYSTEMS AND STRUCTURE OF SiF.

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Introduction.

IN the course of an enquiry on the dissociation energies of certain molecules we came to deal with the SiF molecule whose spectrum has been investigated by Johnson and Jenkins¹. Reference to this work showed that the nature of the electronic levels was left undecided and this is not surprising, since the work was done when the theory of band spectra was yet in the making. Johnson and Jenkins found a large number of bands, which on account of their appearance were divided into five groups, the so-called α , β , γ , δ and ϵ bands. They were further able to propose a vibrational analysis of the α - and β -bands, which showed, that these two systems involve a common final level, which being the lowest was regarded as the ground state of the molecule. This ground-level appears to have been regarded in literature as a $^2\Sigma$ level. Theoretical considerations which have been developed in recent years, we mean for instance the basic idea of the method of molecular orbitals of building up the configuration of the molecule by putting in electrons step by step in their energetical order, indicate, that the ground-level of the molecule SiF should rather be a $^2\Pi$ level. In view of this and the fact that the whole of the spectrum has not been systematised, we undertook a new vibrational analysis of these bands. It was not thought necessary to repeat the experiments, because of the accurate and careful data of Johnson and Jenkins. Further, the excellent reproductions of the bands, which they have published served us as well as original plates. We have been able to show that the analysis of the β -bands proposed by these authors happens to be numerically roughly correct, but the transition involved is $^2\Sigma \rightarrow ^2\Pi$. The analysis of the α -bands, however, needs considerable revision and shows that they should be regarded as a $^2\Pi \rightarrow ^2\Pi$ transition. The γ -bands which could not be analysed before

¹ R. C. Johnson and H. G. Jenkins, *P. R. S.*, 1927, 116(A), 327.

TABLE I
Analysis of β -Bands

v'	v''	0	1	2	3	4	5	6
0	P	34539.3 (10)	33693.7 (10)	32859.3 (4)	32030.7 (2)	31210.8 (0)		
	Q	555.7 (10)	708.4 (10)	870.1 (5)	043.1 (2)	..		
	P	701.8 (4)	856.1 (10)	33021.0 (3)	193.7 (0)	380.2 (0)		
	Q	716.6 (9)	869.3 (10)	031.9 (6)	(212.4) (2)	..		
1		35539.0 (8)	32212.4 (2)	..	
		557.5 (8)	224.8 (2)	31411.1 (0)	
		703.8 (8)	34856.5 (2)	34019.8 (7)	193.0 (3)	376.2 (1)	..	
		719.1 (7)	871.9 (2)	032.3 (8)	204.1 (5)	391.9 (2)	578.5 (0)	
2	c	36532.2 (2)	35685.9 (4)	31607.4 (0)
	c	548.3 (3)	33217.4 (3)	32405.5 (2)	764.1 (0)
		693.1 (3)	..	34185.1 (3)	34185.1 (3)	364.8 (2)	556.4 (1)	..
		711.3 (2)	863.9 (5)	196.8 (4)	196.8 (4)	376.0 (4)	569.2 (2)	..
3			36666.2 (2)	35830.5 (1)
			685.2 (3)	848.5 (6)
			828.7 (3)	993.0 (2)	35161.3 (1)	34348.3 (1)	33537.2 (0)	..
			846.4 (2)	36007.3 (2)	..	360.1 (1)	548.4 (1)	32745 (2)
4				36801.3 (2)	35976.2 (0)	
				820.7 (3)	
				964.1 (2)	36138.7 (0)	35321.6 (2)	..	
				982.0 (1)	153.1 (0)	
5				36937.3 (1)	36937.3 (1)	
				955.9 (2)	955.9 (2)	
				37100.3 (2)	37100.3 (2)	
				116.8 (1)	116.8 (1)	
6				37074.1 (1)	35480.8 (1)	
				208.0 (0)	..	
				235.7 (0)	..	

are due to ${}^2\Sigma \rightarrow {}^2\Pi$. There is evidence to show, that the headless bands of the δ group also belong to this system. The final ${}^2\Pi$ level of all the three systems is the same, ϵ , the ground-level of the molecule. Only the bands in the ϵ system have not been classified but we have something to say about these later on. We now propose to give an account of the analysis, we have been able to make.

The β -Bands.

The analysis of this system is given in Table I. The bands form a well-defined system of close doublets in the region 3200 to 2680 A.U., and are degraded towards the shorter waves. In reality the close doublets are the P and Q heads associated with ${}^2\Pi_{1,2}$ and separated from a similar P and Q doublet of ${}^2\Pi_{3,2}$ by a frequency difference of about 161 cm^{-1} . The analysis in the main yields similar constants to those given by Johnson and Jenkins because of the fact that the doublet separation is also roughly equal to the difference between the vibration frequencies of the initial and final states².

The essential difference between the present analysis and the earlier one is, that whereas only two heads were ascribed to each band formerly, we now know that a ${}^2\Sigma \rightarrow {}^2\Pi$ transition should give rise to four heads, in this case two P and two Q heads, and these are shown in their proper places in the present analysis. This has necessitated a rearrangement of the vibrational quantum numbers used by Johnson and Jenkins and therefore a revision in the vibrational constants. Incidentally the present analysis does not indicate any pronounced perturbation, which according to the older one was present. The perturbations, if any, are only met with in the α -bands, where also it is difficult to decide this point because of the absence of Q heads, the data being obtained from R heads only. We believe that this rearrangement of the bands also removes the slight discrepancies in the isotopic observations, mentioned by Johnson and Jenkins.

The data for the mean vibrational differences of the ground state are given in Table VII later on together with those derived for the same level from other systems. The mean vibrational differences for the initial state are :—

² We cannot say anything definitely on the difficulty experienced by Johnson and Jenkins regarding the isotopic heads, because the data are not included in their paper. It is quite possible that the introduction of half quantum numbers will solve this difficulty especially if we remember that $(\rho-1)$ for Si^{28}F and Si^{30}F is fairly large (-0.0136) and ν_0 will be shifted by about 80 cm^{-1} .

TABLE II.
 $\Delta G'(v)$, β -Bands

	0-1	1-2	2-3	3-4	4-5
P-P	999.5	990.8	980.2	973.2	961.4
Q-Q	1001.6	991.1	982.6	973.1	963.7

Using the values obtained from the Q heads the following equation is derived from the weighted means for the second differences:—

$$\nu_{\text{head}} = \frac{34555.7}{716.6} \left\{ + (1006.4 v' - 4.8 v'^2) - (852.0 v'' - 4.7 v''^2) \right\}.$$

The γ - and the δ -Bands

The structure of the γ -bands is similar to that of the β -bands. Each band consists of two P and two Q heads and they appear as double-headed bands because of the overlap of successive sequences, the electronic separation, which is the same as in the β -bands, being greater than the difference between the two vibrational frequencies. Table III contains

TABLE III
Analysis of γ -Bands.

$v' \setminus v''$	0	1	2	3	4	5
0	P 39341.2 (3) Q 369.1 (5) P 503.2 (5) Q 531.5 (6)	38496.6 (2) 522.8 (5) 659.7 (3) 683.8 (5)	37864.4 (1) 685.3 (3) 827.3 (2) 847.2 (3)			
1		39370.3 (7) 401.7 (3) .. 562.3 (3)	38536.5 (3) 565.0 (2) 702.8 (2) 727.1 (2)	.. <i>vd</i> 37735.9 (1) 876.3 (2) 897.1 (2)		
2			.. 39430.0 (3) .. 591.4 (1)	38574.8 (2) 602.4 (2) 740.6 (2) 764.5 (2)	37760.7 (1) <i>d</i> 781.8 (1) 926.0 (1) 945.0 (1)	
3					38609.7 (2) <i>c</i> 638.8 (2) 775.9 (2) 800.7 (2)	37798.8 (1) .. 968.2 (1) ..
4						.. 38685.6 (2) 809.8 (2) <i>d</i> 834.5 (1)

an analysis of these bands. As will be seen from the data given in Table VII later, there is little doubt, that the final state of these bands is the same as that of the β -bands. The mean vibrational differences for the initial state are:—

TABLE IV
 $\Delta G'(v)$, γ -Bands.

	0-1	1-2	2-3	3-4
P-P	873.8	864.3*	849.5	841.6*
Q-Q	879.3	865.8	855.9	

These data are not so numerous as in the β system and therefore the vibrational function derived is likely to be in error. For instance, the values marked with asterisks are each obtained by a single observation. Even in the Q heads already the 2-3 frequency is rather a mean of two values only, one of which is obtained from bands which are either confused or diffuse. Using the values weighted with due consideration to these facts, and taking for the final state the same function as for the β -bands, we obtain the following equation —

$$\nu_{\text{head}} = \frac{39369.1}{531.5} \left\{ + (885.5 v' - 6.2 v'^2) - (852.0 v'' - 4.7 v''^2) \right\}.$$

If, however, the data on the P heads are used, $\omega'x'$ comes out to be only 5.3 and this would make a big increase in the dissociation energy. We shall deal with this later. The electronic separation, obtained as a mean from the Q heads, comes out to be 161.8 cm^{-1} , as compared to 161.1 cm^{-1} the β -bands. This we take as evidence for the $^2\Sigma$ nature of the upper level though of course a $^2\Delta$ term with an insignificant electronic separation would just as well be valid.

We now come to the δ -bands which are described to be headless. The two vibrational functions of the γ -bands are close and the initial decreases more rapidly than the final so that already for the band (3, 0) and (3, 1) they will be practically identical and bands involving such transitions will be headless. The accuracy of measurement naturally cannot be very great and within such probable limits of inaccuracies it will be possible to include these headless bands in Table III. We have not included them, however, there, but the following Table V will show how the strongest of them could be classified on this basis.

TABLE V.
Classification of the Stronger δ -Bands.

ν	Intensity	Classification
39498	3	Q_1 (4-4)
39674	2	Q_2 (4-4)
40261	2	Q_1 (2-1)
40337	1	Q_1 (5-4)
40424	4	Q_2 (2-1)
40510	4	Q_2 (5-4)
41100	3	Q_1 (3-1)
41276	5	Q_2 (3-1)
41959	4	Q_1 (3-0)
42121	1	Q_2 (3-0)
39311.2	3	P_1 (0-0)
39369.1	5	Q_1 (0-0)

Included in
Table III.

The α -Bands.

These bands are easily the most complicated. As shown in Table VI each band has again four heads. This apparently suggests a transition in which Λ changes by 1. This would mean the existence of Q heads which, however, are certainly not present as is clear from the partial rotational analysis given by Johnson and Jenkins. Further corroboration of this fact has been supplied recently by Badger and Blair³ who have reported a revision of the rotational analysis. This band, which is thus analysed, is that at 22886.2 cm^{-1} . It consists of two strong branches, has an unmistakable null-point at a distance of about 18 cm^{-1} from the head and therefore cannot be the head of a strong Q branch which it would be if the transition involved a change of Λ . It is certainly therefore an R head and if any Q heads were present, they would have been near about the null-point. Such heads at an average distance of about 18 to 25 cm^{-1} are present for instance in the

³ R. M. Badger and C. M. Blair, *Phys. Rev.*, 1935, 47, 881.

β - and γ -bands, but are completely absent here. According to our analysis this band is a (3, 3) band and the abnormal intensity is certainly due to the fact that it is not a single band but has superimposed upon it another band, probably a (4, 4) band with about the same wavelength

The Q heads being ruled out, the transition must be one involving no change in Λ and since the final state of these bands is identical with that of the β - and γ -bands, the transition involved is $^2\Pi \rightarrow ^2\Pi$. The existence of four heads in such a transition is unusual but is possible if the Ω selection rule no longer holds. This happens, when one of the terms approaches more to Hund's case *b*. We believe that such a condition obtains here and that the four observed heads are due to $^5R_{21}$, R_1 , R_2 , and $^0R_{12}$ branches respectively. A similar case occurs in the ultra-violet bands of O_2^+ , where, however, the strong $^5R_{21}$ and $^0R_{12}$ branches do not go to form heads. That they form heads in SiF is apparently due to the fact that the heads are formed at relatively high *J* values.

It is not obviously possible to deduce a strict value for the electronic separation of the R heads because this cannot be constant from band to band. If we take the mean separation between R_1 and R_2 heads, we obtain 132.2 cm.^{-1} which gives for the upper $^2\Pi$ state an electronic separation of $(161.1 - 132.2) = 28.9 \text{ cm.}^{-1}$. This incidentally shows, that the upper $^2\Pi$ state is also regular and not inverted. From the low magnitude of the electronic separations in both the upper state and particularly in the ground state, it appears as if the latter one, or, may be, both terms approach Hund's case *b*. The vibrational differences for the final state are included in the following Table VII along with those of the β - and γ -bands. From this comparison it can be concluded that the final levels of all the three systems are identical

TABLE VII
Comparison of $\Delta G''(v)$ values

	0-1	1-2	2-3	3-4	4-5	5-6	6-7
β -Bands P-P	845.7	835.9	826.6	816.8	809.8	(792.3)	—
Q-Q	847.3	838.2	828.0	817.7	811.5	(800.8)	—
γ -Bands P-P	844.1	832.8	827.1	814.4			
Q-Q	847.0	836.5	828.7	820.1			
α -Bands R-R	839.5	833.7	823.1	817.8	808.4	(802.4)	(790.8)

The vibrational differences of the Q heads of the β - and γ -bands agree very well indeed and those of the α -bands generally as well as can be expected from the values which are obtained as means of all the four R heads. The value 839.5 for the first vibrational difference in these bands as compared with the same difference obtained in the other bands indicates, if real, a perturbation in the first two levels of the initial state of the system.

The mean vibrational differences for the initial state are given in the following table:—

TABLE VIII
 $\Delta G'(v)$, α -Bands

0—1	1—2	2—3	3—4	4—5	5—6
667.5	651.7	639.6	628.7*	601.8*	597.9*

On account of the absence of Q heads the mean differences thus obtained are not equally reliable and particularly those marked by asterisks are obtained from a few measurements only. It is quite likely therefore that the vibrational function derived from these values will be slightly in error. Due consideration to this fact will be given later when we come to discuss the dissociation products. Using for the final vibrational function that obtained from the more accurate data of the β -bands, we derive the following equation to represent the bands of the α system:—

$$\nu_{\text{head}} = \left. \begin{array}{l} 23613.4 \\ 573.9 \\ 448.4 \\ 411.6 \end{array} \right\} + (674.4v' - 6.9v'^2) - (852.0v'' - 4.7v''^2).$$

Unclassified Bands.

The analysis given includes all the bands in the β and γ systems of Johnson and Jenkins except one or two, which are very weak; most of the strong bands listed in the so-called δ system are shown also as part of the γ system and the weaker ones probably belong also to the same system. Among those listed in the α system all the strong ones are accounted for but there are a few with an intensity less than about 2 which cannot be fitted in the scheme. The bands thus unaccounted for are not only all weak but most of them are also diffuse or confused with other bands and some of them are measured approximately only. A more careful investigation would, we believe, be necessary to assign them properly either as main bands of the system or as isotopic heads.

The only system which we have not been able to analyse is the ϵ system. These bands are degraded towards the violet and very few of them are strong. We believe the data are not sufficient, but from the fact that they are degraded towards the violet, the vibrational frequency in the initial state will be bigger than that of the ground state, which, we believe, will be identical with that of the other systems. We offer further remarks about this system later.

Intensity Distribution.

The intensity distribution of all three systems is shown in Tables IX (*a* to *c*). In the β -bands the intensity distribution is roughly analogous to that shown in Fig. 16 (*a*) in Jevons' *Report*⁴ with a pronounced bias towards the initial level. This is in conformity with the greater energy of dissociation which the molecule has in the initial state. The α -bands, on the other hand, correspond to a distribution given in Fig. 16 (*c*) of Jevons' *Report* with a pronounced stability of the lower state. The γ -bands show an intensity distribution of the type given in Fig. 16 (*b*) of the above *Report*. On account of the near equality of the ω values, the bands are confined to a few long sequences, not involving big changes of v . This indicates that our interpretation of the headless bands is very probably correct. We believe also that the energy of dissociation of the upper state is more likely to be equal to or slightly bigger than that of the lower state, and not smaller than

TABLE IX.
Intensity Distribution
(*a*) β -Bands.

$v' \backslash v''$	0	1	2	3	4	5	6
0	8	10	5	2	0		
1	8	2	8	5	2	0	
2	3	5		4	3	2	0
3		3	3	1vd	1	1	2vc
4			2	0	2vd		
5				2		1vd	
6					0		

⁴ W. Jevons, *Report on Band Spectra*, London, 1932, p. 69.

TABLE IX. (b) γ -Bands.

$\begin{smallmatrix} v'' \\ \diagdown \\ v' \end{smallmatrix}$	0	1	2	3	4	5
0	5	4	2			
1		4	2	2		
2			2	2	1	
3					2	1
4						2

TABLE IX. (c) α -Bands.

$\begin{smallmatrix} v'' \\ \diagdown \\ v' \end{smallmatrix}$	0	1	2	3	4	5	6	7	8
0	8	8							
1		6	7	2	4				
2			6	7	3	5			
3				6	6	1	4		
4					8	8	2	2	
5					4		6	2	1
6								3	

it, as obtained from extrapolation of the above vibrational function. The correlation of the products of dissociation of the upper state to atomic terms also points in this direction, as will be seen later.

Dissociation Energy and Electronic Configuration.

The energies of excitation and dissociation of the observed terms of the molecule are given in volts together with the excitation energies of the dissociation products in the following Table X and in the diagram of Fig. 1.

TABLE X.
Dissociation and Excitation Energy.

Term	ν_0 (volts)	D (volts)	$\nu_0 + D' - D''$
$X^2\Pi$	0	4.77	0
$A^2\Pi$	2.91	2.04	0.18
$B^2\Sigma$	4.28	6.51	6.03
$C^2\Sigma$	4.88	3.90	4.01

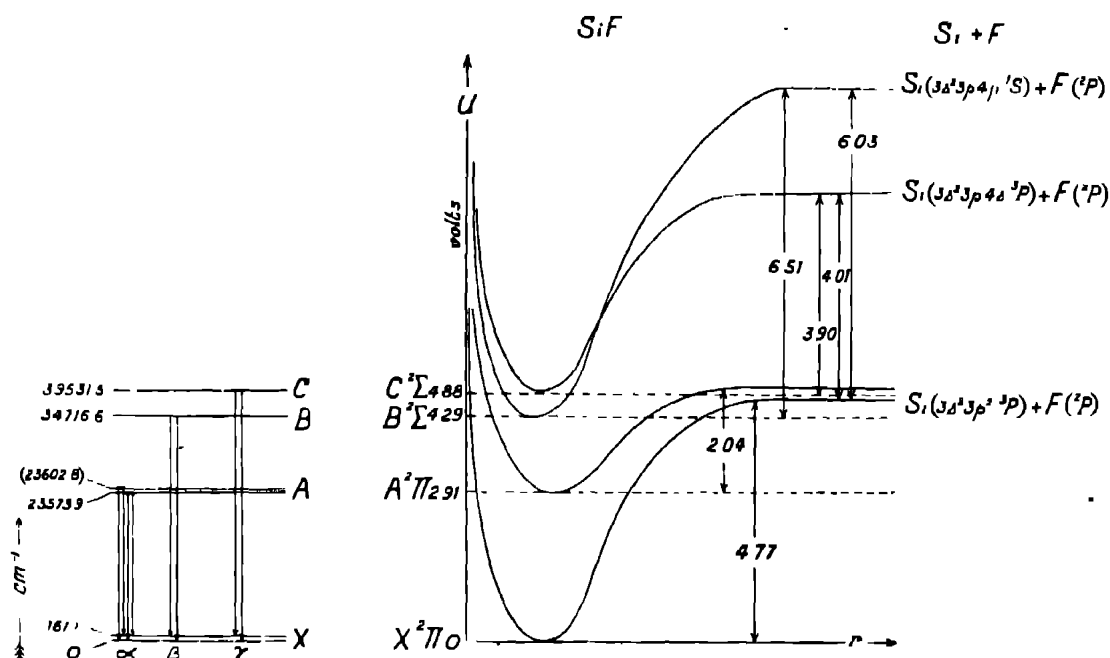


FIG. 1.

We now proceed to discuss the correlation of the molecular levels to those of the separated atoms and thus select the most probable electronic configurations of the molecule in its four states from the various possible ones. The ground state $X^2\Pi$ of the molecule arises from unexcited atoms $\text{Si } (3s^2 3p^2, ^3P) + \text{F } (2s^2 2p^5, ^2P)$.

From these configurations we derive the following structure.

$$\dots \sigma^2(s) \sigma^{*2}(s) \pi^4(p) \sigma^2(p) \pi^*(p) \dots X^2\Pi$$

The level $A^2\Pi$ involves the same unexcited atoms; the difference of 0.18 volts between the dissociation products is well within the errors of extrapolation or, if real, might be attributed to the electronic separation

of one or both of the constituent atoms. It must, however, be remembered that the constants for this level are derived from the R heads and the vibrational frequency differences obtained are fewer as well as less satisfactory than those of the $B^2\Sigma$ and $X^2\Pi$ levels of the molecule. Still, there appears to be little doubt, that the curve runs to the same convergence limit as that of the ground-level. These considerations show that the electronic configuration of this state does not involve a change in the principal quantum number of the electrons. Furthermore, it cannot be the $\pi^*(p)$ electron, which without change in the principal quantum number can be transferred to the $\sigma^*(p)$ group only, because the resulting molecular term would then be $^2\Sigma$. Therefore we have only to consider the excitation of one of the inner p -electrons. The following are the three possibilities in this case —

$$\dots\dots\pi^4(p) \sigma(p) \pi^{*2}(p) \dots\dots\dots (1)$$

$$\dots\dots\pi^4(p) \sigma(p) \pi^*(p) \sigma^*(p) \dots\dots\dots (2)$$

$$\dots\dots\pi^3(p) \sigma^2(p) \pi^{*2}(p) \dots\dots\dots (3)$$

The first of these is to be ruled out because it does not give rise to a $^2\Pi$ level. It is difficult to choose between the possibilities (2) and (3) which are both probable. Since the energy of dissociation in this state is considerably less than in the ground state without an increase of the principal quantum number of the electrons, it is one of the bonding electrons, that is excited. From the point of view of the electron pair bond theory of linkage, the electron from one of the groups $\sigma^2(p)$ or $\pi^4(p)$ whichever contains a p -electron contributed by the Si atom, will be bonding, the second p -electron of Si being the odd electron in the group $\pi^*(p)$. From the other view-point both groups are non-promoted and therefore bonding.

The level $B^2\Sigma$ is interesting. The constants for this level are particularly more reliable than those for $A^2\Pi$ and $C^2\Sigma$. We expect therefore that the extrapolated energy of dissociation, which is derived from the constants deduced from the Q heads is accurate. It clearly indicates a strong increase in bond energy. From analogy with many other molecules, in which a similar situation obtains we ascribe this increase to the excitation of the odd $\pi^*(p)$ electron, which has been shown in numerous cases to have nothing to do with the linkage but to disturb it. Indeed the energy of 6.03 volts between the dissociation products of this and the normal state is in complete accord with 6.16 volts which is the difference

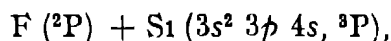
$$2s^2 3p^2, ^3P - 3s^2 3p 4p, ^1S,$$

of Si. Accordingly the $\pi^*(p)$ odd electron is taken to one of the $\sigma(p)$ groups of the next principal quantum number, probably the non-promoted one. We therefore assign the following configuration to this level:—

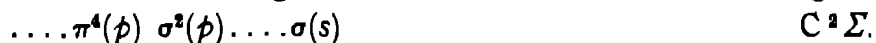
$$\dots\dots\pi^4(p) \sigma^2(p) \dots\dots\sigma(p) \qquad B^2\Sigma.$$

This therefore furnishes another example in favour of the pair-bond view. Extending this view we should expect some other terms with increased energy of dissociation arising from configurations of the atom Si such as $3p\ 4s$, 3P which also would give structures of the molecule in which the odd electron is excited. Such a molecular term originates at 4.9 volts (the energy of excitation of 3P) and if we assume a dissociation energy similar to that of $B\ ^2\Sigma$, we obtain for the excitation of the molecule about 3 volts. It is not unlikely that the bands of the so-called ϵ system with 23898 cm^{-1} as one of its strongest bands belong to such a state. These bands are degraded towards the shorter waves, as we would expect them to be on account of increased energy of dissociation.

The $\Delta G'(v)$ values for the $C\ ^2\Sigma$ level are not so numerous and therefore not so satisfactory as those of the β -bands. They should, however, be more reliable than those for the $A\ ^2\Pi$ level because here we can deduce them from the Q heads. We remark here simply that the data on P heads yield for $\omega'x'$ 5.3 while those on Q heads give 6.2. The dissociation energy is extrapolated from the latter values and it appears as if it is slightly too low. As a matter of fact, there is no term in Si and of course none in F which can be correlated to 4.01 volts which is the excitation of the products of dissociation of this level. We therefore attribute this level to



which gives an excitation energy of 4.90 volts. Indeed, if we would use for $\omega'x'$ the value 5.3 obtained from data on P heads, we get a dissociation energy of 4.6 volts and an excitation energy of 4.7 volts for the products of dissociation. On this basis the electronic configuration would contain a $\sigma(s)$ electron of the next higher main quantum number which has been a p -electron in the $X\ ^2\Pi$ level. It cannot be an electron from the $\sigma^2(p)$ group because the resulting configuration $\sigma\pi\sigma$ cannot give a $^2\Sigma$ level. Therefore it must be one of the premoted or non-premoted π -electrons. By assuming an excitation energy of 4.90 volts for the dissociation products the energy of dissociation of the $C\ ^2\Sigma$ level becomes 4.81 volts. This value is almost identical if not higher than that for the ground-level. This is not improbable in view of the fact that the γ -bands are shaded towards the shorter wave side, which certainly means a decrease in the internuclear distance and probably, but not always, an increase of the bond energy. In view of this, we rather believe that it is the $\pi^*(p)$ electron, which is excited to the next higher $\sigma(s)$ group and the electronic configuration would then be the following:—



The theoretical implications will be discussed at greater length in a forthcoming paper.

THE DESIGN OF FALLS WITH REFERENCE TO UPLIFT PRESSURE.

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Introduction

IN a series of investigations,^{1, 2} carried out in the Institute, it was definitely established that the distribution of uplift pressure under hydraulic works such as weirs and dams follows the same law as the distribution of electrical potential in conductors. Having established this fact, the method is now employed for the investigation of uplift pressure under hydraulic works. The details of the method are described in the papers referred to above. Since then a number of standard cases,^{3, 4} and actual weirs⁵ have been investigated by this method.

In the present paper, it is proposed to give an account of the investigation of the uplift pressure under hydraulic works on porous foundations, such as are built in canals and rivers

Construction of Falls

Fig. 1 represents the cross-section of a fall with a length L_1 for the upstream apron, L_2 for the downstream apron, depth d_1 for the fall and d_2

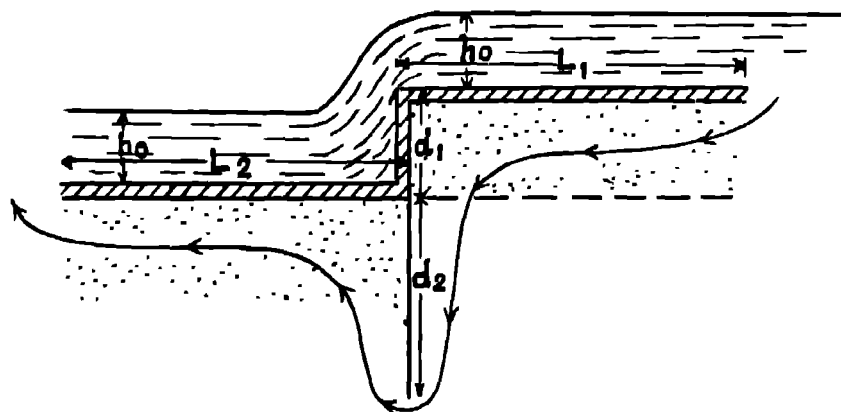


FIG. 1

for the sheet pile. There is a depth h_0 of water upstream and a similar depth of water downstream. As illustrated in the figure, there is a difference of head equal to d_1 and due to the seepage flow taking place through the porous subsoil, this head exerts an uplift pressure on the masonry. If there is a lock and there is only water on the upstream side then the head d_1 increases to $d_1 + h_0$, since there is no water downstream. It is necessary to know the residual pressures at any point and its distribution for purposes of design

Results

Two series of experiments were carried out. In the first series, the lengths of downstream apron were varied, the fall d_1 and the length of the sheet pile d_2 being kept constant. The length, L_1 of the upstream apron in the model was maintained at four inches, the fall d_1 one inch and the length of the sheet pile d_2 4" throughout this series. In the second series, the lengths of the downstream and upstream aprons and the depth of the fall were kept constant and the length of the sheet pile varied from 0 to 5". Nine cases of the former series and eight cases of the latter series were investigated and complete pressure contours were plotted. Fig. 2 shows one such case as an illustration. The pressure contours of the remaining sixteen cases

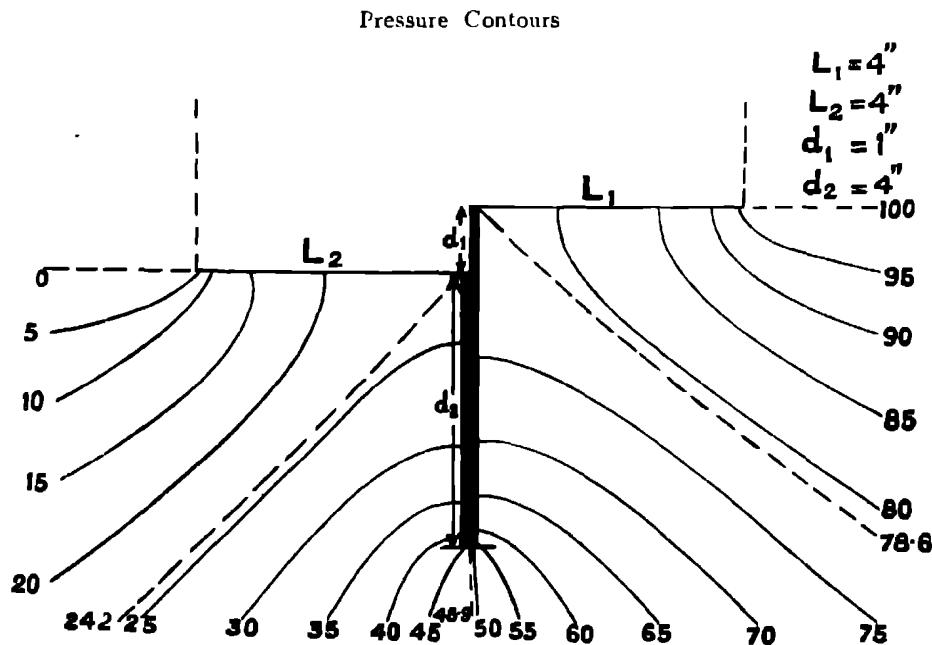


FIG. 2.

are not shown here as the types are similar. From the engineering point of view, the hydraulic gradient along the underside of the masonry is the most

important consideration, since it is this gradient that measures the uplift pressure at any point.

Fig. 3 shows the pressure distribution under the masonry for different values of L_2 . The drop in pressure caused by the sheet pile is shown by the discontinuities in the curves. The percentage drop in pressure is marked for each graph.

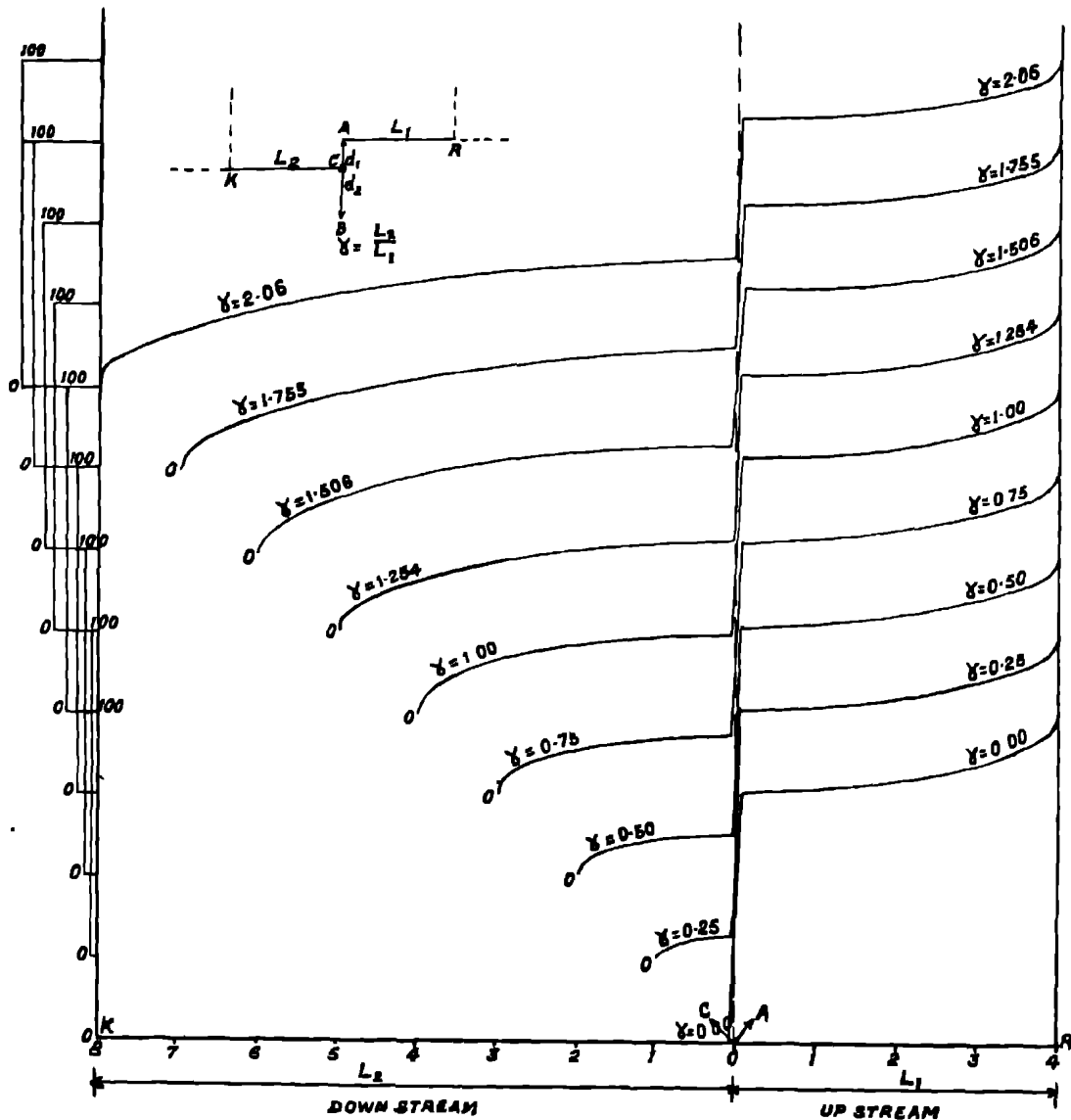


FIG. 3.

While the total drop of pressure caused by the sheet pile is shown by the discontinuity of lines in Fig. 3, the actual distribution along the sheet pile is shown in Fig. 4. It may be seen from this figure that while L_2

changes from 0 to 8" in the model, the changes of pressure at the upstream sides of the sheet piles are not very considerable. This point is of importance in connection with the application of the results to design.

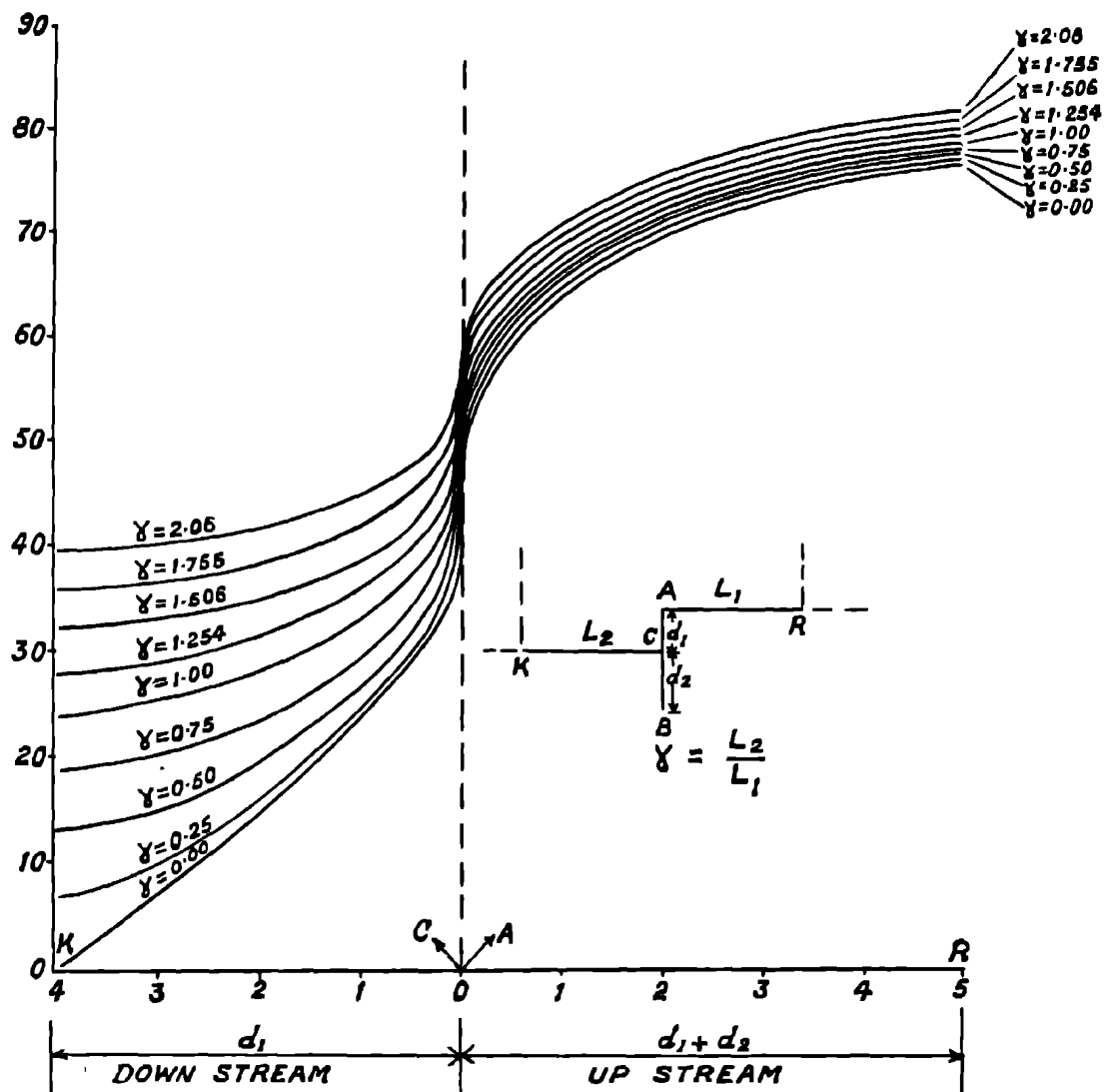


FIG. 4

Fig. 5 shows the distribution of pressure when the lengths d_2 of the sheet pile change from 0 to 5". L_1 and L_2 were maintained at 7" in all the experiments referred to in this figure. Again while the total drop of pressure along the sheet pile is given by the discontinuity in the curves in Fig 5, the nature of the distribution of pressure along the sheet pile is given by Fig. 6. As is seen in Fig. 6, the dotted line joining the pressures

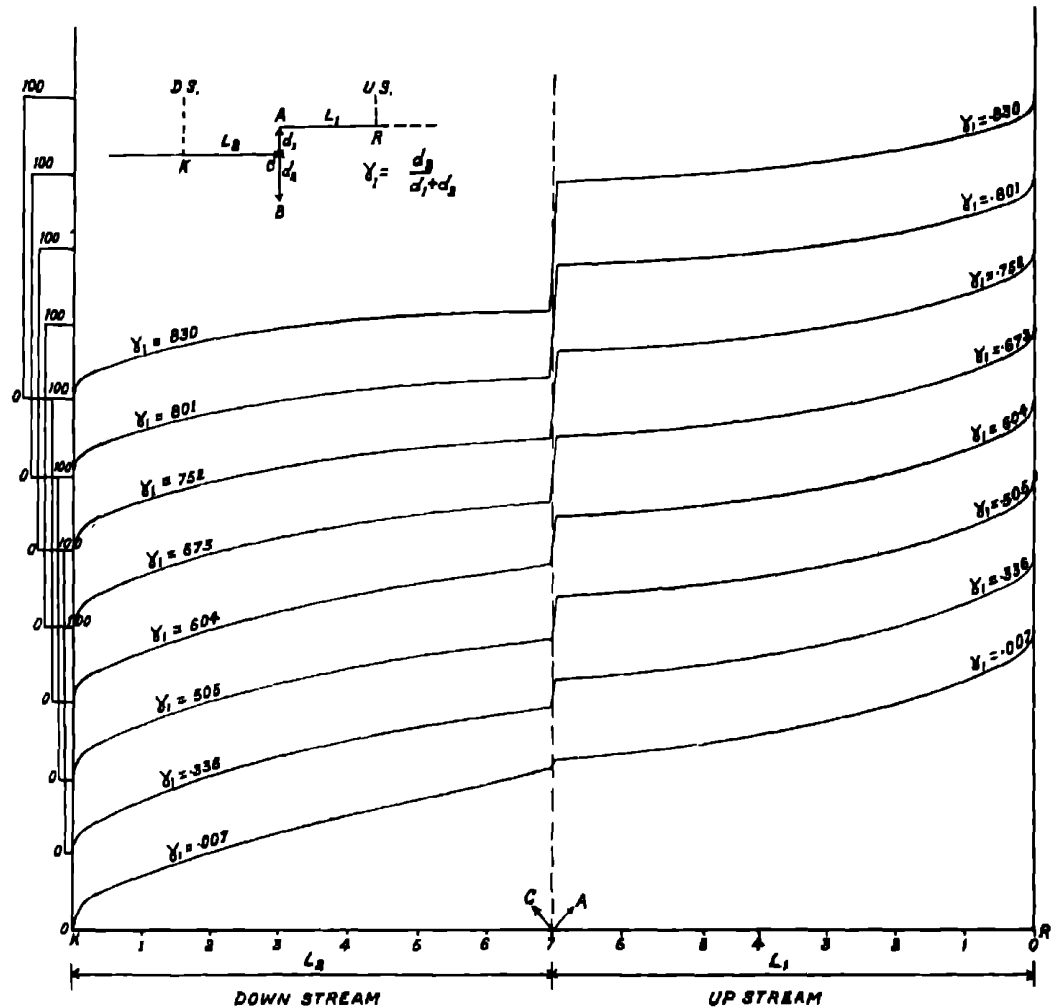


FIG. 5.

at the corners A and C (*i.e.*) the ends of the pressure distribution curves, has only a very small curvature. The value of the pressures at A and C for any particular combinations of $d_2/d_1 + d_2$ can thus be obtained from this curve, by interpolation.

On the Design of Falls.

When a fall is to be designed for a particular combination of floor and sheet pile, the best method is to subject the design to an experimental examination. In the Punjab, this is always done.

The results of the present investigation can be used for the ordinary combinations of sheet pile and floor, but it is not possible to apply the results so far obtained to all possible designs. There is no accurate theoretical expression by means of which the uplift pressure can be derived for every such case of a fall. Comparison of the present data shows that

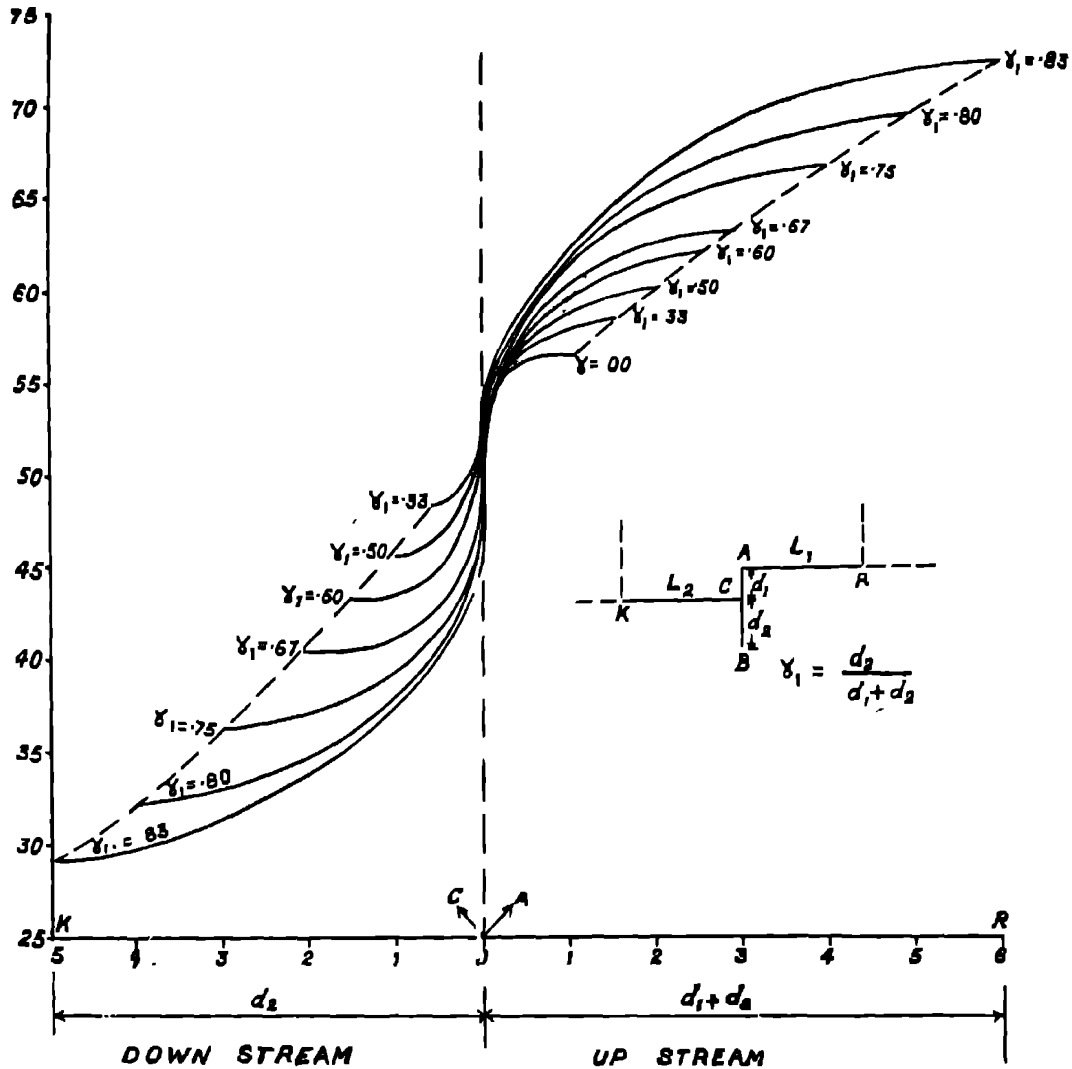


FIG. 6.

the pressure distribution for the type of works indicated by the model in Fig. 1, corresponds very nearly with those of a single sheet pile case under a flush floor, when the fall d_1 is small compared with L_1 and L_2 and sheet-pile not at the heel or toe. For such a case, namely, a sheet pile under a simple floor, as is shown in Fig. 7, a complete theory has been worked out by Weaver.⁶ The expression to find the pressure on the base of the dam is, according to him,

$$p(x, y) = \frac{p_0}{\pi} c(x, y) = \frac{p_0}{\pi} \cos^{-1} \left[\frac{d(\chi - \lambda) \pm \sqrt{\chi^2 + d^2}}{d\lambda} \right]$$

the origin $x = 0$ corresponding to the position of the pile and the value of x increasing from the upstream to the downstream side. In this expression

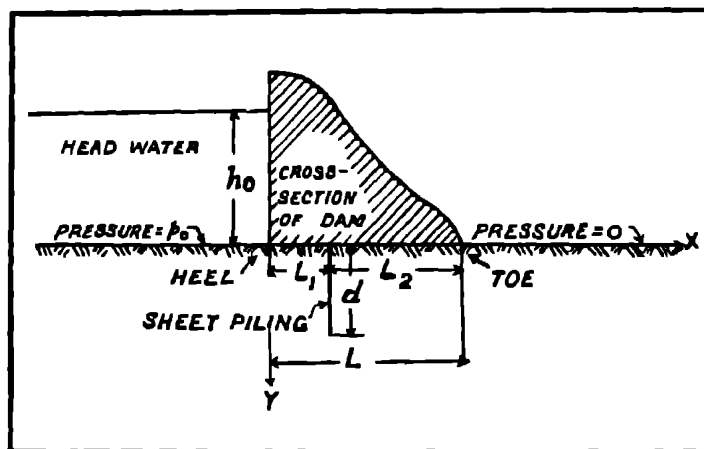
$$\chi = \sqrt{1 + a_1^2}$$

$$\lambda = \frac{\sqrt{1 + a_1^2} + \sqrt{1 + (a - a_1)^2}}{2}$$

$$a_1 = \frac{L_1}{d} \quad \text{and} \quad a = \frac{L}{d}$$

d = depth of the sheet pile and

L = length of the floor. (See Fig. 7.)



Reproduced from the *Journal of Mathematics and Physics*,
June 1932 (W. Weaver)

FIG. 7.

If it is desired to obtain an approximate value of the uplift pressure without recourse to an experiment, in the absence of a general solution Weaver's expression may be applied to the case of falls as has already been stated. In applying this equation to the case of a fall, $d_1 + d_2$ may be regarded as the length d of the pile for purposes of calculation on the upstream side and d_2 for the length of the pile on the downstream side. The justification for so doing lies in the fact that, as seen from Fig. 4, the changes in L_1 between limits shown in the figure do not affect the nature of the distribution of pressure on the upstream side by any appreciable amount.

Adopting such a method of calculation as is indicated here, the results of a comparison between the theory and experiment are shown in the table. The extreme variation is about 8%. It is generally much less as can be seen by comparing columns 3 and 4, and 7 and 8 in the table. This degree of accuracy is sufficient for practical purposes, since a factor of safety is usually introduced in the design.

Comparison between the Theoretical and Experimental Values.

(For Positions of A and C, see Inset in Fig. 3.)

UPSTREAM SIDE P_A denotes pressure at A				DOWNSTREAM SIDE P_C denotes pressure at C			
a	a_1	P_A Theoretical	P_A Experimental	a	a_1	P_C Theoretical	P_C Experimental
0.800	0.80	77.2	77.0	1.00	1.00	0.0	0.0
1.000	0.80	77.3	77.1	1.25	1.00	7.3	6.8
1.200	0.80	77.6	77.4	1.50	1.00	13.8	12.9
1.400	0.80	78.0	78.2	1.75	1.00	19.8	18.7
1.600	0.80	78.5	78.6	2.00	1.00	25.0	24.2
1.800	0.80	79.1	79.3	2.25	1.00	29.5	27.9
2.000	0.80	79.7	79.9	2.50	1.00	33.3	31.9
2.200	0.80	80.2	80.7	2.75	1.00	36.6	37.1
2.400	0.80	80.7	81.7	3.00	1.00	39.5	39.4
<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;"> L_2 varying ; L_1, d_1 and d_2 constant. </div> </div>							
9.33	4.67	56.7	58.4	28.00	14.00	47.7	48.2
7.00	3.50	58.8	60.2	14.00	7.00	45.5	45.6
5.60	2.80	60.9	62.1	9.33	4.67	43.3	43.3
4.67	2.33	62.9	63.2	7.00	3.50	41.1	40.4
3.50	1.75	66.5	66.9	4.67	2.33	37.1	36.2
2.80	1.40	69.7	69.7	3.50	1.75	33.5	32.3
2.33	1.17	72.6	72.6	2.80	1.40	30.2	29.2
<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;"> d_2 varying ; L_1, L_2 and d_1 constant. </div> </div>							

Other Considerations

One important point in the design of such works is the pressure gradient at the toe. When the water escapes from beneath the work in an upward direction, the incoherent material from below the masonry is removed by the water. This causes cavities to form under the works and frequently such a work will fail at the toe. If a sheet pile is driven at the toe, this pressure gradient flattens as can be shown both experimentally and theoretically. The toe has, therefore, to be protected by a suitable length of piling or depressed masonry. The correct length of this piling or depression has to be estimated taking various considerations such as stratification head, etc. into account. When once the length of this piling is fixed, there is a specific length for the floor, which will give the maximum safety. Any extra length does not add to the safety as might be expected.

An important factor is the geological stratification with its consequent modification of the pressure distribution. When stratification is known to occur, the pressure distribution can only be determined by an experiment

in which the stratification is reproduced. The effect of stratification will be appreciable only if it occurs near the work. As has been pointed out by Weaver, "the distortion which a sheet piling produces in the lines of flow does not extend as far from the piling as one might expect. The distortion due to the piling extends a distance in all directions equal, roughly to the piling depth. The interest in this observation lies in the strong suggestion that non-homogeneities in the foundation material very likely are effective in disturbing seepage flow only in a neighbourhood, whose dimensions are roughly twice those of the non-homogeneity. One has thus a crude means of judging, when and to what extent is applicable an analysis based on homogeneity."

Summary.

In this investigation the uplift pressures under hydraulic works on porous foundations, such as are built at the falls in canals and rivers, have been determined

Two series of experiments have been carried out and the pressure distributions have been obtained for ordinary combinations of sheet pile and floor. A method of obtaining the pressure distribution approximately by the application of theory has also been indicated

Our thanks are due to Dr. F. McKenzie Taylor, the Director, for his keen interest in the problem

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STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS—PART III.

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(Communicated by Mr S Bhagavantam.)

1 Introduction

IN Parts I and II of this series (Sundara Rama Rao, 1936) the dependence on the temperature of the molar refractivities and the anisotropic coefficients of the optical polarisation field in some typical non-associating liquids has been studied. A brief discussion was given on the significance of the results to the subject of light-scattering. In this part, it is proposed to extend the above investigations to some typical associated liquids. The results already available in the case of water are examined and three other liquids, namely, nitrobenzene, acetic acid and formic acid are studied here for the first time.

2 Experimental.

In this investigation, a Pulfrich refractometer has been used for the measurement of refractive indices. This instrument has a double advantage over the Abbe refractometer in that it yields greater accuracy in measurement and can be used for such corrosive liquids as formic and acetic acids.

The refractometer having been tested for zero error, the prism is connected to a copper heater supplied with a steady flow of water from a constant pressure head. Two accurate thermometers reading to 0.1° over the ranges $0-50^\circ$ and $50^\circ-80^\circ$ are provided with the instrument together with a correction chart for the readings. Measurements of refractive indices are made with an electric sodium vapour lamp and all the values therefore refer to λ 5893 A.U.

3. Results.

The refractive indices and the densities at different temperatures which are already available in the case of water* are given in Table I. The molar refractivities calculated from these data are shown in the last row of this table. Tables II, III and IV contain the refractive indices obtained in the present investigation at different temperatures for formic acid, acetic acid and nitrobenzene respectively. The densities given in these tables are also taken from *I. C. T.* and the molar refractivities are calculated therefrom at all the temperatures at which the refractive indices have been measured.

* *Landolt-Bornstein Tabellen* and *I. C. T.*, Vol. III.

TABLE I.
Molar Refractivity of Water.

Temp.	0	10	20	30	40	50	60	70	80
Ref. Index	1.33381	1.33360	1.33330	1.33202	1.33069	1.32908	1.32718	1.32516	1.32300
Density	0.99987	0.99973	0.99823	0.99568	0.99225	0.98807	0.98324	0.97781	0.97183
Mol. Refractivity	3.71447	3.71288	3.71238	3.71196	3.71122	3.71043	3.70907	3.70871	3.70894

TABLE II
Molar Refractivity of Formic Acid

Temp	30	35	40	45	50	55	60	65	70
Ref. Index	1.36725	1.36543	1.36343	1.36146	1.35958	1.35798	1.35585	1.35365	1.35140
Density	1.20873	1.20259	1.19644	1.19028	1.18409	1.17789	1.17167	1.16541	1.15913
Mol. Refractivity	8.55426	8.55975	8.56152	8.56396	8.56851	8.57916	8.57855	8.57662	8.57365

TABLE III.
Molar Refractivity of Acetic Acid

Temp.	30	35	40	45	50	55	60	65	70	75
Ref. Index	1.36963	1.36816	1.36680	1.36525	1.36343	1.36137	1.35958	1.35753	1.35532	1.35304
Density	1.0388	1.0335	1.0282	1.0229	1.0175	1.0120	1.0065	1.0009	0.9952	0.9895
Mol. Refractivity	13.0591	13.0793	13.1033	13.1212	13.1320	13.1361	13.1492	13.1550	13.1567	13.1560

TABLE IV.
Molar Refractivity of Nitrobenzene

Temp.	10	15	20	25	30	35	40	45	50	55	60	65
Ref Index	1.55700	1.55450	1.55242	1.54947	1.54720	1.54487	1.54173	1.54018	1.53796	1.53580	1.53361	1.53123
Density	1.21312	1.20817	1.20322	1.19826	1.19329	1.18833	1.18335	1.17837	1.17339	1.16840	1.16341	1.15841
Mol. Refractivity	32.6610	32.6732	32.7058	32.6959	32.7196	32.7400	32.7203	32.7803	32.8068	32.8366	32.8650	32.8839

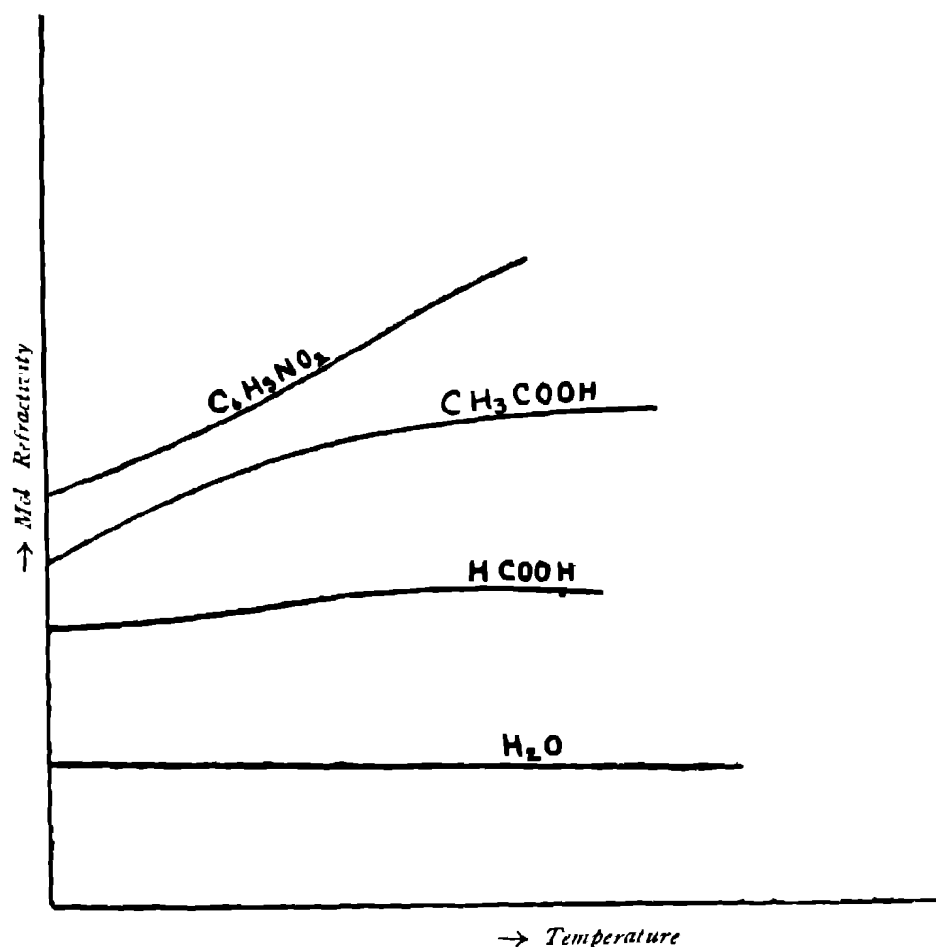


FIG. 1.

4. Some Remarks

The curves drawn in Fig. 1 represent graphically the variation in the molar refractivity with temperature and hence the extent to which the Lorentz law breaks down in these cases. The group of liquids studied in this part are of a different type and hence behave in a manner which is slightly different from that of the liquids studied in Part I. The molar refractivity of acetic and formic acids *increases slowly up to a certain temperature and then begins to diminish*. The behaviour of nitrobenzene is similar to that of benzene. It is interesting to note that the changes in the molar refractivity of water are of a much smaller order of magnitude than those exhibited by other liquids. The curve shows that it may be regarded as practically constant in the range 0–80° C. It must however be remarked that a close examination of the results given in Table I reveals a slight but definite and progressive *diminution* in the molar refractivity of this substance as well.

5. *Significance of the Results to the subject of Light Scattering.*

As indicated in Part II, the results are intimately connected with the depolarisation of scattered light exhibited by these liquids at different temperatures. As the group now under investigation consists of associating molecules, it will be of interest to examine this aspect of the question also.

With the exception of water, the refractive indices of the corresponding vapours are not available for the liquids studied in this paper. Hence the method of calculation of the coefficients of the anisotropic polarisation field becomes slightly altered. If A' , C' and C'^* represent the effective principal optic moments for a liquid molecule at a particular temperature and p_1 , p_2 and p_3 the corresponding coefficients of anisotropy of the polarisation field surrounding the molecule in the liquid state, the following relationships hold.—

$$\frac{n_l^2 - 1}{4\pi\nu_l} = \frac{A' + 2C'}{3} \quad \dots (1) \quad \frac{r_l}{6 - 7r_l} = \frac{\nu_l (A' - C')^2}{45 kT\beta \left(\frac{n_l^2 - 1}{4\pi} \right)^2} \quad \dots (2)$$

and

$$\left. \begin{aligned} \frac{4\pi + p_1 (n_l^2 - 1)}{4\pi + p_2 (n_l^2 - 1)} &= \frac{1 + 2\sqrt{\delta_l}}{1 - \sqrt{\delta_l}} \times \frac{1 - \sqrt{\delta_v}}{1 + 2\sqrt{\delta_v}} \text{ if } A > C \\ \frac{4\pi + p_1 (n_l^2 - 1)}{4\pi + p_2 (n_l^2 - 1)} &= \frac{1 - 2\sqrt{\delta_l}}{1 + \sqrt{\delta_l}} \times \frac{1 + \sqrt{\delta_v}}{1 - 2\sqrt{\delta_v}} \text{ if } A < C \end{aligned} \right\} \quad \dots (3)$$

$$p_1 + 2p_2 = 4\pi \quad \dots \quad \dots \quad \dots \quad \dots (4)$$

$$A' = A \left(1 + p_1 \frac{n_l^2 - 1}{4\pi} \right) \quad \dots (5) \quad C' = C \left(1 + p_2 \frac{n_l^2 - 1}{4\pi} \right) \quad (6)$$

n_l , ν_l and r_l represent respectively the refractive index, number of molecules per c.c. and the depolarisation of the transversely scattered light in the liquid state. A knowledge of these quantities together with that of the compressibility of the liquid at a particular temperature enables us to calculate A' and C' at that temperature for the various molecules from equations (1) and (2). After substituting the observed values for δ_l and δ_v the coefficients p_1 and p_2 are calculated from equations (3) and (4). Making use of the relationships (5) and (6) the values of A and C , the principal optic moments of the molecule in the vapour state are deduced from those of A' , C' and p_1 , p_2 . The values of p_1 and p_2 at every temperature are thereafter calculated by the method indicated in Part II of this series with the help of equations (3) and (4) of that part. The coefficients of the anisotropic polarisation field so derived are made use of in calculating the depolarisation of

* This assumption is strictly valid only for axially symmetric molecules and can be regarded as merely an approximation in these cases.

TABLE V.
Acetic Acid.

$\delta_D \times 10^3 = 25.9$; $\delta_I \times 10^3 = 34.3$ $A = 6.8461 \times 10^{-24}$; $C = 4.2371 \times 10^{-24}$

Temp.	30	35	40	45	50	55	60	65	70	75
n_D	1.36963	1.36816	1.36680	1.36525	1.36343	1.36137	1.35958	1.35753	1.35532	1.35304
p_1	4.994	5.167	5.374	5.531	5.627	5.669	5.788	5.845	5.872	5.876
p_2	3.786	3.700	3.596	3.518	3.470	3.449	3.389	3.361	3.347	3.345
p_1/p_2	1.319	1.396	1.494	1.572	1.622	1.644	1.708	1.739	1.754	1.757
$\beta \times 10^{12}$	104	132.5
100 <i>r</i> calc.	48.0	44.0
100 <i>r</i> obs.	42.8	34.3

TABLE VI.
Nitrobenzene

$\delta_D \times 10^3 = 54.7$; $\delta_I \times 10^3 = 32.5$ $A = 7.1187 \times 10^{-24}$; $C = 16.5078 \times 10^{-24}$

Temp.	10	15	20	25	30	35	40	45	50	55	60	65
n_D	1.55700	1.55450	1.55242	1.54947	1.54720	1.54487	1.54173	1.54018	1.53796	1.53580	1.53361	1.53123
p_1	6.315	6.303	6.256	6.281	6.249	6.222	6.265	6.169	6.132	6.088	6.046	6.021
p_2	3.126	3.132	3.155	3.143	3.159	3.172	3.151	3.199	3.218	3.239	3.260	3.276
p_1/p_2	2.020	2.013	1.983	1.998	1.978	1.962	1.988	1.928	1.906	1.880	1.855	1.838
$\beta \times 10^{12}$	47	55
100 <i>r</i> calc.	68.8	65.8
100 <i>r</i> obs.	66.0

the transversely scattered light in the liquid state by the formula already given in Part II. The results so calculated at certain temperatures are compared with the experimental values available from the work of Ramachandra Rao (1927) and Krishnan (1936) in Tables V and VI. As the necessary data are not available for formic acid, it has not been dealt with here

6. Discussion of Results.

It is seen from the tables that in the case of acetic acid, the anisotropy of the polarisation field increases with increasing temperature in the entire range studied. This behaviour is quite peculiar and is presumably attributable to the presence of large molecular aggregates, which break up with rise of temperature. Their presence in acetic and formic acids has an independent confirmation from the recent work of R. S. Krishnan (1936).

We will now interpret the results regarding the variation of molecular refractivity on the basis of the Lorentz law as modified by Raman and Krishnan (1928).

$$\frac{n_l^2 - 1}{n_l^2 + 2} = \frac{4\pi}{3} \nu_l \frac{A+B+C}{3} \left(1 + \nu_l \frac{A\sigma_1}{3} + \frac{B\sigma_2}{3} + C\sigma_3 \right)$$

which transforms into

$$\frac{n_l^2 - 1}{n_l^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N \frac{A+2C}{3} \left(1 + \nu_l \frac{A\sigma_1 + 2C\sigma_2}{3} \right)$$

where $\sigma_1 = \rho_1 - \frac{4\pi}{3}$ etc. The factor responsible for the variation in the molar refractivity is $\nu_l (A\sigma_1 + 2C\sigma_2)$. Ordinarily, this factor may easily be shown to be negative and its numerical value tends to diminish with increasing temperature. As such the molar refractivity normally increases with increasing temperature, examples being C_6H_6 , C_6H_{14} , etc., studied in Part I. In the case of acetic acid however $\sigma_1 > \sigma_2$ and since $\sigma_1 + 2\sigma_2 = 0$ we can write the variable factor as $\nu_l \sigma_1 (A - C)$ which is easily seen to be *positive*. Further, as the temperature rises σ_1 *increases*. Both these features are exceptional and may, to some extent, be regarded as consequences of the fact that the observed value of δ_ν for acetic acid is less than the observed value of δ_l . Apart from the uncertainty involved in applying the equations to such a case, a further complication arises on account of the presence of large groups which may break up with rise in temperature. The observed curve in acetic and formic acids must be regarded as the resultant of all these factors and it is not surprising that at a certain temperature the molar refractivity ceases to increase and begins to diminish.

7 Summary.

The molar refractivity is found to increase with temperature in nitrobenzene and diminish, although only slightly, in the case of water. In the cases of acetic and formic acids, it increases up to a certain temperature and then begins to diminish. The coefficients of anisotropy of the optical polarisation field are calculated in the cases of acetic acid and nitrobenzene. In the former, the polarisation field becomes more and more anisotropic whereas in the latter it becomes more and more isotropic with increasing temperature.

The author is highly thankful to Mr. S. Bhagavantam for his helpful guidance in the work.

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VARIATION OF INTENSITY OF SCATTERED LIGHT WITH TEMPERATURE.

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1. Introduction.

It has been noticed in this laboratory by Veerabhadrarao* that the intensity of the Rayleigh scattering in certain liquids such as formic acid behaves in an unexpected manner in as much as it diminishes with increasing temperature. This observation, though of a qualitative nature, was quite definite and is contrary to what may be expected and to what has been observed in normal cases such as benzene.

The aim of the present investigation is to experimentally determine the intensity of the transversely scattered light at different temperatures in some typical liquids. The experimental results are compared with the values calculated on the basis of the formula given by Raman and Krishnan (1928) and an attempt has been made to explain the different behaviours exhibited by different types of liquids.

A similar investigation was undertaken earlier by Ramachandrarao (1927). He experimented upon a number of organic liquids including the fatty acids. The method of measurement was, however, based on a visual examination of the scattered light. Recently, Krishnan (1936) also carried out certain experiments wherein he had obtained the intensity of scattering at different temperatures using a photo-electric cell. In the present investigation a spectrograph has been used, thus separating the Rayleigh scattering from the Raman lines, and the method of obtaining a scale of intensity marks by varying the slit widths has been used in computing the relative intensities of the scattered light at different temperatures.

2. Experimental.

The liquid under investigation is contained in an ordinary Wood's tube with slight modification and of internal diameter $1\frac{1}{2}$ inches. The scattered light is observed through a small window in one of its ends with

* Thesis submitted to the Andhra University, 1935.

suitable arrangements to eliminate all parasitic light. The liquid is illuminated by condensing the light from a six-inch quartz mercury arc by means of a large glass condenser. The tube and the liquid inside are heated by means of a specially constructed electric furnace. The temperature of the liquid is measured with a thermometer dipped into the liquid through an opening in the upper side of the tube. The furnace is calibrated prior to the experiment and the different current strengths required to keep the temperature of the liquid constant at different stages, are determined. The slit of the spectrograph is made wide enough, so that, the image includes also that part of the orientation scattering which separates out as rotational wings.

The same exposure is given at different temperatures without altering the other arrangements. A set of intensity marks is recorded on the plate by the method of varying slit widths. The intensity of the incident light has been kept constant by feeding the mercury arc from a 220-volt battery. In the present investigation, benzene, acetic acid, formic acid and nitrobenzene have been studied. All measurements in the first three cases refer to λ 4358 whereas in nitrobenzene they refer to λ 5460. The density-log intensity curves have been obtained in the usual way for each plate by running the plate through a Moll microphotometer and the relative intensities of the scattering at different temperatures are obtained from these curves. In each one of the cases, three different plates have been obtained and the results given in the following tables represent the mean values of the different sets of readings.

3. Results

In the last column of Tables I, II, III and IV, the intensities observed at different temperatures are given. The figures are only relative and have no absolute significance. In the first three cases, data regarding the refractive index, compressibility and depolarisation at different temperatures have also been given, so far as available. Compressibility data are taken from *International Critical Tables*, Vol III for all liquids.

The depolarisation values for benzene, nitrobenzene and acetic acid are taken respectively from Sundara Rama Rao (1936), Ramachandra Rao (1927) and Krishnan (1936). Refractive indices have all been obtained from the recent work of Sundara Rama Rao (1936). In such cases where data are not available at the required temperatures, the temperature variation graphs are drawn and the values deduced therefrom.

TABLE I.

Benzene †

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1.4950	102.0	38.9	10.00	10.00
40	1.4884	110.0	37.4	10.42	10.47
50	1.4820	119.0	36.3	10.82	11.15
60	1.4752	121.0	34.8	11.14	11.68
70	12.09

TABLE II.

Nitrobenzene. ‡

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1.54720	52.0	69.0	12.88	12.88
40	1.54173	55.0	68.0	12.48	12.02
50	1.53796	56.5	66.0	11.19	11.75
60	1.53361	59.0	63.0	9.76	11.51
70	11.44
80	11.15
90	11.02
100	10.78
110	10.42
120	9.77

† The results obtained are in good agreement with those reported earlier by Ramachandra Rao.

‡ The results obtained in this case are not in agreement with those reported earlier by Ramachandra Rao.

TABLE III. *Acetic Acid*.§

Temp. ° C.	Refractive index	Compressibility	Depolarisation %	Intensity calculated	Intensity observed
30	1.36963	97.0	17.8	13.80	13.80
40	1.36680	104.0	44.1	13.19	14.17
50	1.36343	111.0	40.8	12.49	14.39
60	1.35958	119.0	38.0	12.14	14.79
70	1.35532	128.0	35.1	11.65	14.58
80	14.85
90	15.10
100	15.72

TABLE IV *Formic Acid* ¶

Temperature ° C.	Depolarisation %	Intensity observed
30	47.5	16.60
40	44.7	15.31
50	41.8	14.32
60	38.8	14.29
70	36.0
80	33.0	13.96
90	30.0	13.80

§ The results obtained in this case are not in agreement with those reported by Krishnan.

¶ Krishnan has also reported a set of diminishing intensities with rise in temperature in this case

A knowledge of these figures will enable us to calculate the intensity of the scattered light that is to be expected at different temperatures from the following relation (Raman and Krishnan, 1928)

$$I = I_0 \frac{\pi^2}{2d^2} \cdot \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 \frac{6 + 6r}{6 - 7r}$$

where I = Intensity of scattered light, I_0 = Incident light; d = distance of the scattering centre from the point of observation; μ = refractive index of the liquid, r = depolarisation; T = Absolute temperature; β = Compressibility; R = Gas constant; and λ = the wave-length.

The values so calculated for benzene, nitrobenzene and acetic acid are shown in column 5 of their respective tables. These figures are also relative and have no absolute significance.

The compressibility data are not available for formic acid and hence similar calculations could not be made in this case. The depolarisation factors at different temperatures (Krishnan, 1936) are however included in Table IV as they will be referred to later

4 Discussion of Results

In the case of benzene, the calculated values and experimental values closely agree with each other. In nitrobenzene, both the calculated and experimental values decrease with rise in temperature but the calculated values decrease more rapidly than the experimental values. In the case of formic acid the intensity as observed experimentally decreases with rise in temperature. For acetic acid, while the observations show that the intensity of scattered light increases with rise in temperature, theoretical calculations show that it decreases with rise in temperature.

The observed results regarding the intensity variation are represented graphically in Fig. 1. The scale chosen does not give any indication of

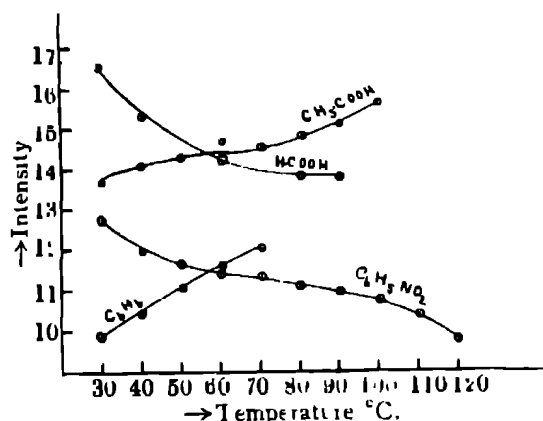


FIG. 1.

the relative scattering powers of the various liquids but is significant only as regards the variation of intensity of the light scattered by any particular

liquid with temperature. The results are somewhat puzzling at first sight as the intensity in benzene and acetic acid increases whereas in formic acid and nitrobenzene, it decreases with increasing temperature. A better insight is obtained into this phenomenon if we separate out the observed aggregate intensity into its constituent parts, namely, the density scattering and the orientation scattering in each case. If we denote the x -component by $2I_x$ and the z -component by $I_z + I_x$ when incident unpolarised light of given intensity is used, then we have (Raman and Krishnan, 1928) :

$$r = \frac{2I_x}{I_z + I_x} = \frac{RT\beta \left(\frac{2n_0}{4\pi} F \right)^2}{N \left(\frac{2n_0}{4\pi} F \right)^2 + \frac{7}{3} n_0 F}$$

It will be seen from the figures given in Tables I to IV that the depolarisation r and the aggregate intensity of scattering are known at a variety of temperatures and hence we can easily evaluate separately the two portions which constitute the aggregate. The results are shown in Table V.

TABLE V

Temperature °C.	Benzene			Nitrobenzene			Acetic acid			Formic acid		
	Aggregate	Density	Orientation	Aggregate	Density	Orientation	Aggregate	Density	Orientation	Aggregate	Density	Orientation
30	10.00	3.93	6.07	12.88	1.48	11.40	13.80	4.13	9.67	10.6	5.02	11.58
40	10.77	4.41	6.36	12.02	1.48	10.54	14.17	4.78	9.39	15.31	5.07	10.24
50	11.15	4.72	6.43	11.75	1.62	10.13	14.31	5.35	9.04	14.32	5.18	9.14
60	11.68	5.15	6.53	11.61	1.87	9.64	14.79	5.97	8.82	14.29	5.77	8.52
70	11.44	2.29	9.15	14.58	6.37	8.21
80	11.15	4.25	6.90	13.96	6.46	7.54
90	13.80	6.90	6.90

The most significant result that is evident from Table V is the fact that in all cases studied, the density scattering steadily increases with increasing temperature. This is in perfect accord with what we should expect. The orientation scattering on the other hand increases with increasing temperature in benzene and diminishes with increasing temperature in nitrobenzene, formic acid and acetic acid. Benzene should be regarded as a normal case and is characterised by the fact that the density

as well as the orientation scattering and therefore the aggregate increase with rise in temperature. The other three liquids, which are associating, are abnormal in that while the density scattering increases as it should, the orientation scattering diminishes thus indicating a decrease in the optical anisotropy of the scattering unit with increase in the temperature. These two counteracting influences may result either in an aggregate increase as in the case of acetic acid or an aggregate decrease as in the cases of nitrobenzene and formic acid. Thus, we may conclude that in liquids studied, as the variations in the density scattering are quite normal in all cases, the differences in the behaviour of the different liquids are to be attributed to the abnormal behaviour of the orientation scattering

5 Summary

The intensity of scattering is found to increase with rise in temperature in benzene and acetic acid and to decrease with rise in temperature in nitrobenzene and formic acid. Such differences in the behaviour of these liquids are only apparent and are attributed to the fact that the scattered beam is ordinarily an admixture of two types, namely, density scattering and orientation scattering. When the aggregate intensity is suitably separated into these two constituent parts, the density scattering is always found to increase with increasing temperature as should be expected whereas the orientation scattering sometimes increases (example is benzene) and sometimes decreases (examples are nitrobenzene, acetic acid and formic acid). The observed effect is an aggregate of these two phenomena.

The author takes it his great pleasure to express his most grateful thanks to Mr. S. Bhagavantam, the Head of the Physics Department for the very keen interest he has taken in his work and the valuable guidance he has rendered

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REFRACTIVITY AND MAGNETIC BIREFRINGENCE OF LIQUID MIXTURES.

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1. Introduction.

STUDIES in magnetic birefringence in mixtures of organic liquids made by Cotton and Mouton (1913), Szivessy (1928) and Chinchalkar (1932) have revealed some interesting features. These authors have found consistently that the observed values do not agree generally with those obtained by calculation with the aid of Langevin's theory. On the basis of the observed results, mixtures could be divided into two classes according as the curves representing the variation of magnetic double-refraction with concentration were either concave or convex towards the axis of concentration compared with the curves drawn on the basis of Langevin's theory.

No satisfactory attempt has been made by any of the above authors to explain these deviations. Chinchalkar alone has given a qualitative description of the phenomena in relation to the variation of magnetic birefringence and optical anisotropy with temperature. He has, however, not attempted to explain these deviations quantitatively.

The present investigation was first undertaken mainly with a view to explain quantitatively the data obtained by Chinchalkar on the magnetic birefringence of liquid mixtures. It may be pointed out here that Chinchalkar made use of Lorentz's additivity relation for determining the refractive index and an analogous relation for the magnetic birefringence in calculating the values of the Cotton-Mouton constant expected for a mixture of a particular concentration. This procedure is open to criticism in both respects as the existence of an anisotropic optical polarisation field is not taken account of either in computing the refractive index or the magnetic birefringence of the mixture. It is felt therefore that the method of calculation should be revised by inserting the observed refractive indices for liquid mixtures in place of the calculated ones and at the same time by making use of the expression for the magnetic birefringence of mixtures derived earlier by the author, which takes into account the anisotropy of the optical polarisation field. With this purpose in view, the refractivity

of a large number of liquid mixtures has been examined at different concentrations and the results in some cases which serve to illustrate the main points in the present investigation are contained in the following pages.

Incidentally it became necessary to examine the data of the refractivity of mixtures by themselves in order to see how far they deviate from Lorentz's law of additivity and how far such deviations are explicable on the basis of an anisotropic polarisation field. From this point of view, Narasimhaiah (1934) already examined the data in the case of two mixtures and came to the conclusion that the observed values are in agreement with Raman and Krishnan's theory.

The author's examination of his own results on the refractivity of the number of mixtures he studied, however, revealed that while the deviations of the observed values from Lorentz's law point to an anisotropic polarisation field, they could not be explained by assuming that the anisotropy of the polarisation field is independent of concentration. Consequently, instead of trying to explain the observed deviations in the refractivity on the basis of Raman and Krishnan's theory, the observed refractivities are made use of in calculating the constants of the anisotropic polarisation field at various concentrations. By inserting the constants so calculated in the modified expression for the Cotton-Mouton constant of a liquid mixture, the observed deviations in the latter could satisfactorily be explained. This procedure, besides explaining for the first time quantitatively the experimental results on the magnetic birefringence of liquid mixtures, furnishes evidence in favour of the view that the anisotropy of the polarisation field in mixtures varies with concentration.

2. *Refractivity of Liquid Mixtures.*

The choice of the liquid mixtures was guided by the list of mixtures already examined by Chinchalkar for magnetic birefringence.

An Abbe refractometer was employed to find the refractive indices of the mixtures at various concentrations. The temperature of the mixture was maintained constant by circulating water through the jackets enclosing the prisms and is noted against each of the mixtures in the following tables. The observed values along with the values calculated on the basis of Lorentz's equation, namely,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{v_1}{v_1 + v_2} \times \frac{n_1^2 - 1}{n_1^2 + 2} + \frac{v_2}{v_1 + v_2} \times \frac{n_2^2 - 1}{n_2^2 + 2}$$

are given in Tables I to VII. In the above equation, n stands for the refractive index of the mixture of components of refractive indices n_1 and n_2 and volumes v_1 and v_2 respectively in a total volume ($v_1 + v_2$) of the mixture.

In all the mixtures studied, it has been observed that the total volume is merely the sum of the volumes of the constituents.

TABLE I

Benzene - CCl_4 mixture at $26^\circ.8 \text{ C}$
 Refractive index of $\text{CCl}_4 = 1.4562$
 „ of Benzene = 1.4960

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1.4902	1.4844	1.4775	1.4709	1.4639
n Lorentz's theory ..	1.4885	1.4820	1.4750	1.4690	1.4626
n Raman and Krishnan theory	1.4894	1.4829	1.4762	1.4696	1.4629

TABLE II.

Toluene - CCl_4 mixture at $28^\circ.2 \text{ C}$
 Refractive index of $\text{CCl}_4 = 1.4554$
 „ of Toluene = 1.4917

Volume of Toluene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1.4869	1.4803	1.4751	1.4688	1.4621
n Lorentz's theory ..	1.4855	1.4795	1.4734	1.4674	1.4614

TABLE III

Nitrobenzene - CCl_4 mixture at $28^\circ.5 \text{ C}$.
 Refractive index of Nitrobenzene = 1.5478
 „ of $\text{CCl}_4 = 1.4552$

Volume of Nitrobenzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
n Observed ..	1.5344	1.5212	1.5053	1.4887	1.4724
n Lorentz's theory ..	1.5319	1.5162	1.5007	1.4853	1.4702

TABLE IV.

CS₂—CCl₄ mixture at 26°.8 C
 Refractive index of CS₂ = 1.6222
 „ of CCl₄ = 1.4562

Volume of CS ₂ in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
<i>n</i> Observed ..	1.5920	1.5622	1.5336	1.5078	1.4820
<i>n</i> Lorentz's theory ..	1.5929	1.5642	1.5365	1.5092	1.4824
<i>n</i> Raman and Krishnan theory	1.5929	1.5649	1.5372	1.5099	1.4829

TABLE V

CS₂—Benzene mixture at 26°.8 C.
 Refractive index of CS₂ = 1.6222
 „ of Benzene = 1.4960

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
<i>n</i> Observed ..	1.5144	1.5334	1.5530	1.5750	1.5972
<i>n</i> Lorentz's theory ..	1.5162	1.5367	1.5574	1.5786	1.6001

TABLE VI.

CS₂—Chlorobenzene mixture at 26°.4 C.
 Refractive index of CS₂ = 1.6224
 „ of Chlorobenzene = 1.5212

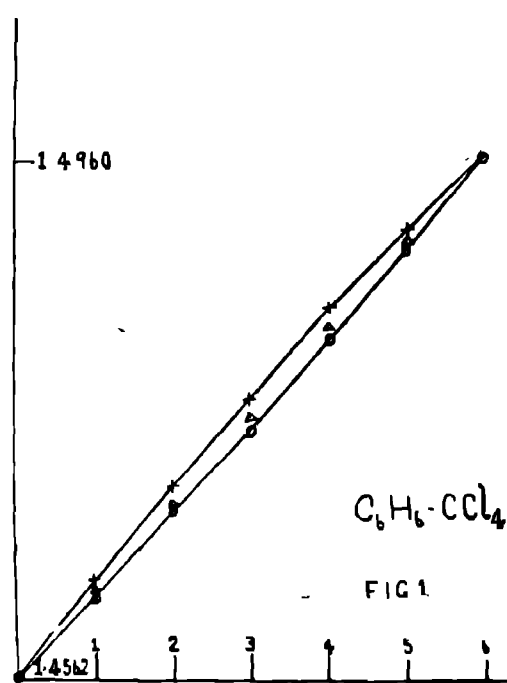
Volume of CS in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
<i>n</i> Observed ..	1.6030	1.5830	1.5664	1.5500	1.5350
<i>n</i> Lorentz's theory ..	1.6050	1.5878	1.5708	1.5541	1.5376

TABLE VII.

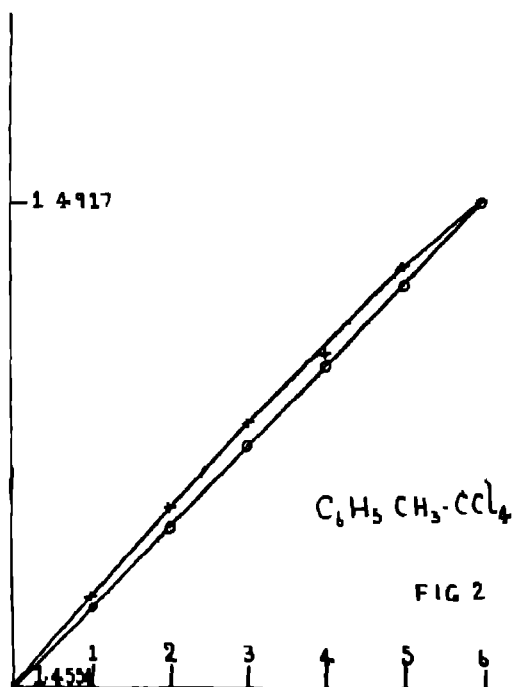
CS₂—Bromobenzene mixture at 27° C.
 Refractive index of Bromobenzene = 1.5560
 „ of CS₂ = 1.6222

Volume of CS ₂ in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
<i>n</i> Observed	1.6095	1.5974	1.5861	1.5754	1.5650
<i>n</i> Lorentz's theory	1.6107	1.5996	1.5886	1.5776	1.5668

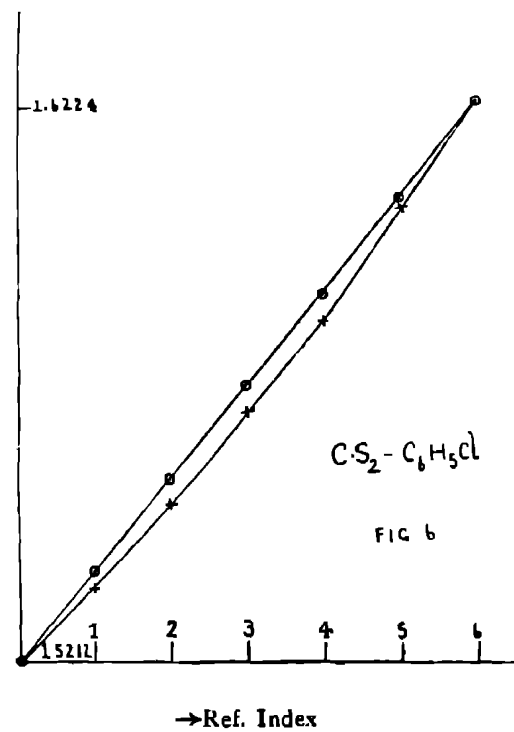
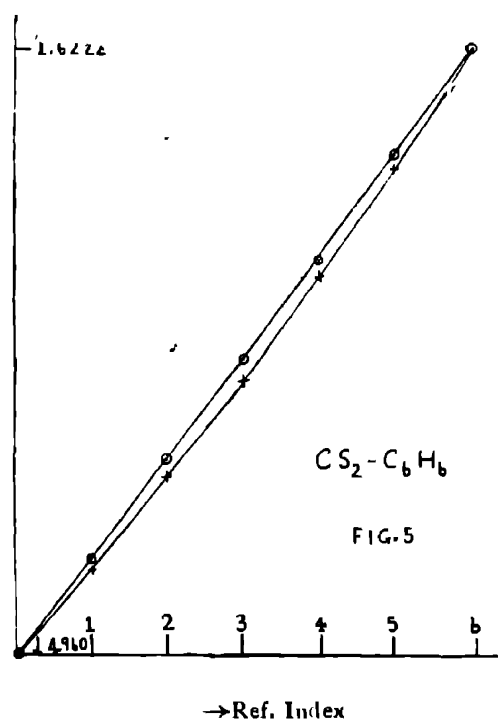
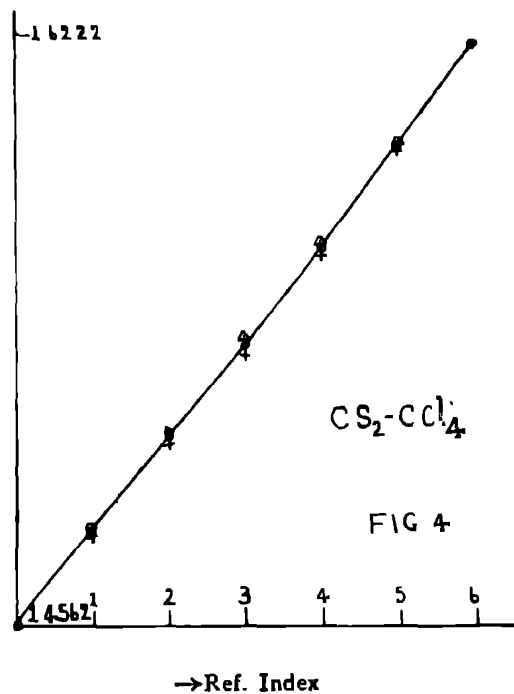
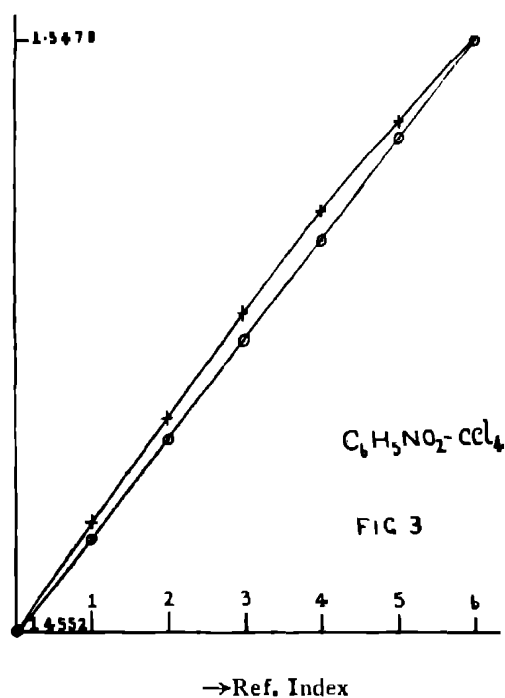
The results contained in the above tables are graphically represented in Figs. 1 to 7. Circles represent values obtained on the basis of Lorentz's

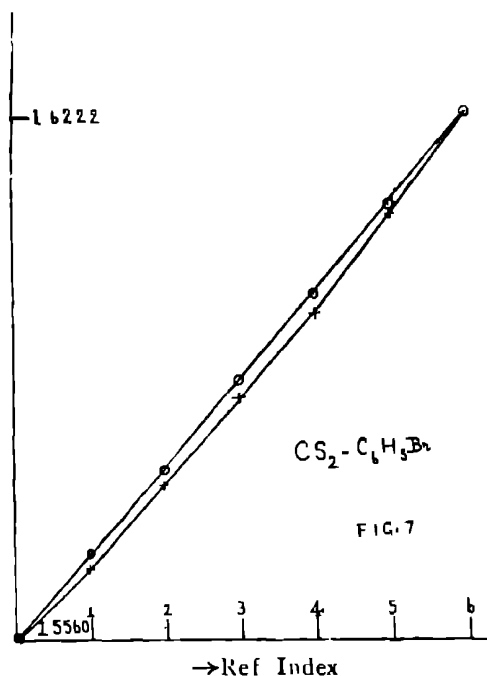


→Ref. Index



→Ref. Index





theory. Crosses represent the observed values. Triangles represent values obtained on the basis of Raman and Krishnan theory.

A glance at the curves will show in the first place, that there are marked deviations from the Lorentz's law in every case and in the second place that these deviations fall into two classes. In the first three cases we find that the observed values are higher than the values calculated. In the last four cases where CS_2 is the common component for the mixtures, we find that the observed values are less than those calculated on the basis of Lorentz's theory.

3. Modification of Lorentz's Expression.

Applying the idea of the anisotropic polarisation field theory, one obtains the following expression for the refractive index of the mixture

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1 (B_1 + B_2 + B_3) + \nu_2 (B_1' + B_2' + B_3')}{3}$$

ν_1 and ν_2 being the number of molecules of the respective components in 1 c.c. of the mixture. B 's represent the effective optic moments. We may express the refractive index in terms of the gaseous optic moments as follows.

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1 (b_1 + b_2 + b_3) + \nu_2 (b_1' + b_2' + b_3')}{3 \{1 - \frac{1}{3}\nu_1 (b_1 p_1 + b_2 p_2 + b_3 p_3) - \frac{1}{3}\nu_2 (b_1' p_1' + b_2' p_2' + b_3' p_3')\}}$$

p 's represent here the constants of the anisotropic polarisation field. If the molecule of one of the components is optically and geometrically

isotropic (e g., CCl_4) and if the molecule of the other component be assumed to possess an axis of symmetry,

$$\frac{n^2 - 1}{4\pi} = \frac{\nu_1 (b_1 + 2b_2) + \nu_2 \cdot 3b'}{3\{1 - \frac{1}{3}\nu_1 (b_1 p_1 + 2b_2 p_2) - \frac{4\pi}{3} \nu_2 b'\}} \quad \dots \quad (1)$$

To make use of the above equation, one requires to know the values of b_1 , b_2 , p_1 , p_2 and b' . The mode of calculating these from the known values of refractive index of the liquid, δ_v and δ_l , is already indicated in a previous paper by the author (1935). To calculate b' for CCl_4 , it is assumed that both the molecule and the polarisation field surrounding the same are isotropic and the Lorentz's formula is applied

Formula (1) is in the first instance made use of to calculate the refractive indices of mixtures on the assumption that values of p_1 and p_2 derived for a pure liquid in the above manner also represent the coefficients of the anisotropic polarisation field in mixtures irrespective of the concentration of the latter. The two typical cases contained in Tables I and IV will suffice to illustrate the disagreement between the observed values and the values so calculated.

As the results with other mixtures are similar, the calculated values in their case are not reproduced in the tables

The results of these calculations are also represented graphically in Figs. (1) and (4) which refer to the mixtures in question

It will be easily noticed from these curves that the introduction of an anisotropic polarisation field with a constant set of p_1 and p_2 does not very much improve the results. There is only a slight improvement in the case of Benzene CCl_4 mixture, whereas in the case of $\text{CS}_2 - \text{CCl}_4$ mixture, the modified theory led to results which are in greater disagreement with experiment.

These facts are very significant as the cases under investigation conform very closely to the requirements of the theory inasmuch as all the three molecules involved, *viz*, CS_2 , CCl_4 and C_6H_6 are nonpolar and hence non-associating. Further the two mixtures chosen are such that one of the constituents in both cases, *viz*, CCl_4 is optically isotropic and is surrounded by an isotropic polarisation field whereas the other constituent which is either CS_2 or C_6H_6 possesses an axis of symmetry. In view of this, the agreement observed by Narasimhaiah (1934) in the case of the mixtures whose data he examined by employing a constant set of p_1 and p_2 at different concentrations must, at best, be regarded as fortuitous.

4. *Variation of the Coefficients of Anisotropy with Concentration.*

Instead of therefore trying to explain the observed refractive indices, it is obviously more fruitful to calculate the values of p_1 and p_2 which will give the observed values of refractive index by making use of equation (1) and the auxiliary equation

$$p_1 + 2p_2 = 4\pi$$

The following tables give the values of p_1 and p_2 so calculated at different concentrations in the case of 3 mixtures

TABLE VIII
Benzene- CCl_4 mixture

Volume of Benzene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$	0.5246	0.5098	0.5081	0.4934	0.4730
$p_2/4\pi$	0.2377	0.2451	0.2460	0.2533	0.2635

TABLE IX.
Toluene- CCl_4 mixture.

Volume of Toluene in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$.5224	.5170	.5022	.4908	.4936
$p_2/4\pi$.2388	.2415	.2511	.2546	.2532

TABLE X
 CS_2 - CCl_4 mixture.

Volume of CS_2 in 6 c.c. of the mixture	5 c.c.	4 c.c.	3 c.c.	2 c.c.	1 c.c.
$p_1/4\pi$.2542	.2416	.2396	.2282	.2292
$p_2/4\pi$.3729	.3792	.3802	.3859	.3854

The general case where both the components are anisotropic is more complicated and is hence not dealt with here.

The inference from the above representation is that we can divide the mixtures into two classes. In the former class of which benzene- CCl_4 is the typical representative, the polarisation field becomes more and more isotropic with diminishing concentration of benzene. In the latter, of which CS_2 - CCl_4 is the typical representative, the polarisation field becomes more and more anisotropic with diminishing concentration of CS_2 . It is interesting to note here that a similar classification of liquid mixtures is also forthcoming from the observations of Chinchalkar on the magnetic birefringence. Those mixtures in which the polarisation field is becoming more and more isotropic with diminishing concentration of the anisotropic constituent show a magnetic birefringence-concentration curve which is concave towards the concentration axis. The other type, in which the polarisation field is becoming anisotropic with diminishing concentration of the anisotropic constituent, shows a birefringence-concentration curve which is convex towards the concentration axis. This close resemblance has furnished the clue for the proper explanation of the observed deviations in magnetic birefringence and this aspect is dealt with in the following section.

5. *Magnetic Birefringence in Liquid Mixtures.*

In an earlier paper, the author (1929) has derived the following expression for the Cotton-Mouton constant of mixtures taking into account the anisotropic polarisation field.

$$C_M = \frac{1}{20} \times \frac{n_0^2 - 1}{n_0 \lambda K T} \times \frac{\nu_1 [(a_1 - a_2) (B_1 - B_2) + \dots] + \nu_2 [(a_1' - a_2') (B_1' - B_2') + \dots]}{\nu_1 (b_1 + b_2 + b_3) + \nu_2 (b_1' + b_2' + b_3')}$$

The letters have the usual significance.

If the molecule of one of the constituents possesses an axis of symmetry (*i.e.*, $b_2 = b_3$; $a_2 = a_3$, etc.) and that of the other is geometrically and optically isotropic, the expression reduces to

$$C_M = \frac{1}{10} \frac{n_0^2 - 1}{n_0 \lambda K T} \times \frac{\nu_1 (a_1 - a_2) (B_1 - B_2)}{\nu_1 (b_1 + 2b_2) + \nu_2 \cdot 3b'}$$

We can express this C_M as a fraction of the C_M of the pure liquid which is the birefringent constituent in the above equation. The C_M of the pure liquid, according to Raman and Krishnan theory, is given by

$$C_M = \frac{1}{10} \times \frac{n_1^2 - 1}{n_1 \lambda K T} \times \frac{(a_1 - a_2) (B_1^* - B_2^*)}{b_1 + 2b_2}$$

Thus the relative birefringence in terms of that of the pure liquid is given by

$$\frac{n_0^2 - 1}{n_0} \times \frac{n_1}{n_1^2 - 1} \times \frac{B_1 - B_2}{B_1^* - B_2^*} \times \frac{(b_1 + 2b_2)}{(b_1 + 2b_2 + \nu_2/\nu_1 \times 3b)} \dots \dots (2)$$

It ought to be noted here that the values of B_1 and B_2 in the above equation, i.e., the effective optic moments of the molecule of the birefringent component in solution are different from B_1^* and B_2^* , the effective optic moments of the same in the pure liquid state. They also change with concentration because in the first place, the optical susceptibility of the mixture is different from that of the pure liquid and is changing with concentration and in the second place, the values of p_1 and p_2 which govern their magnitudes as we have seen above also change with concentration.

With this precaution, values of the relative birefringence in the case of three mixtures, as shown below, are calculated and shown along with the values calculated on the basis of a formula used by Chinchalkar and derived earlier by Bergöhlm (1917), Szivessy (1921). The latter is as follows and is

derivable from equation (2) by putting $p_1 = p_2 = \frac{4\pi}{3}$

$$\text{Relative } C_m = \frac{v_1}{v_1 + v_2} \times \frac{n_1}{(n_1^2 + 2)^2} \times \frac{(n_0^2 + 2)^2}{n_0}$$

Chinchalkar, in his calculations, made use of n_0 derived from Lorentz's additivity relation and as such similar procedure has been adopted in calculating the values in column 3 of the following tables. This would mean that so far as the values in column 3 are concerned, the anisotropy of the optical polarisation field has not been taken account of either in computing the refractive index or the Cotton-Mouton constant. On the other hand, values in column 2, are derived from the observed refractivities and on the basis of the author's expression for C_m which takes into account the anisotropy of the optical polarisation field.

TABLE XI

Benzene- CCl_4 mixture

Partial volume of Benzene ..	0.833	0.667	0.500	0.333	0.167
Rel. birefringence calculated (author) ..	0.862	0.724	0.547	0.380	0.200
Rel. birefringence calculated (Chinchalkar) ..	0.829	0.660	0.492	0.327	0.163

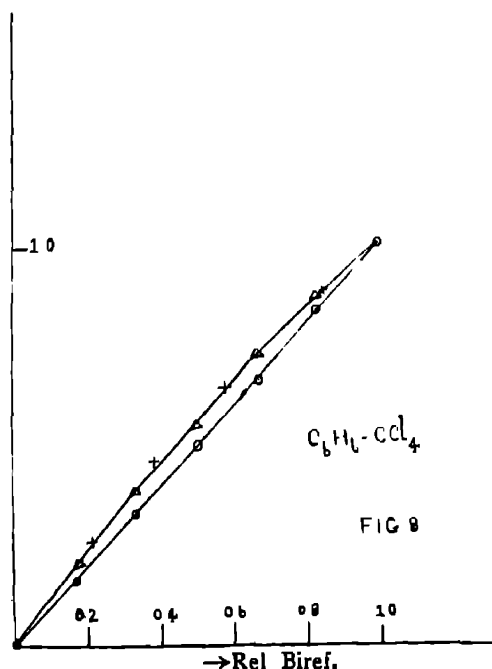
TABLE XII. Toluene- CCl_4 mixture.

Partial volume of Toluene ..	0.832	0.667	0.500	0.333	0.167
Rel. birefringence Calc. (author)	0.843	0.688	0.542	0.369	0.184
Rel. birefringence Calc. (Chinchalkar) ..	0.809	0.645	0.481	0.319	0.159

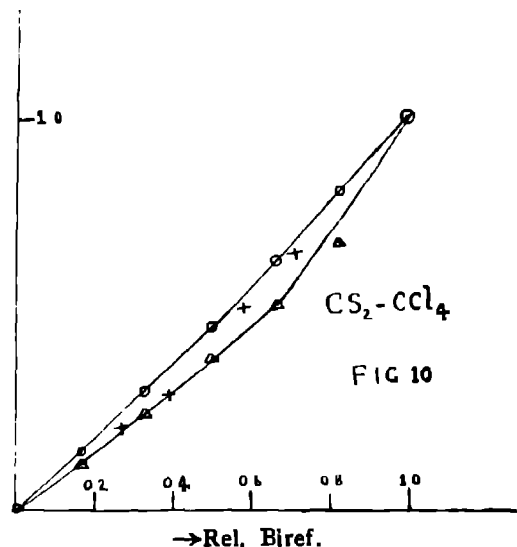
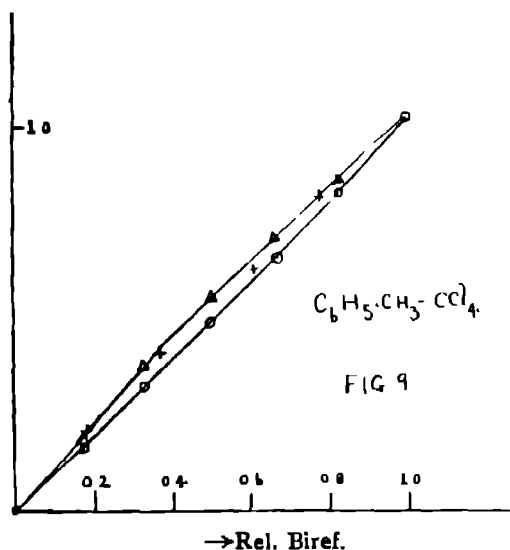
TABLE XIII. CS_2 - CCl_4 mixture.

Partial volume of CS_2 ..	0.833	0.667	0.500	0.333	0.167
Rel. birefringence Calc. (author)	0.685	0.525	0.387	0.251	0.126
Rel. birefringence Calc. (Chinchalkar) ..	0.814	0.637	0.468	0.306	0.150

The above values are calculated for the concentrations at which the refractivities have been measured. It may be noted that these concentrations are somewhat different from those employed by Chinchalkar. Such a difference does not however matter as the results are ultimately represented graphically in Figs 8 to 10.*



* In these figures, crosses represent observed values, circles represent values obtained on the basis of Chinchalkar's expression and triangles represent values obtained on the basis of author's expression.



The agreement between the values calculated according to the author's expression and the observed ones in the case of benzene- CCl_4 and toluene- CCl_4 mixtures is excellent. In the case of CS_2 - CCl_4 mixture, two of the observations lie on the author's theoretical curve while the other two lie away from it. Even here the agreement can be regarded as fair, as in the first place, the character of the observational curve, is satisfactorily brought out by the theory employed by the author and in the second place good agreement is found between two of the observed results and the corresponding theoretical results. As the other points are somewhat erratic, they may be due to experimental error.

There is one case, however, *viz*, nitrobenzene CCl_4 mixture which has not come within the scheme of the explanation offered in the present investigation. The magnetic birefringence-concentration curve of this mixture is convex towards the axis of concentration, while the refractivity curve is concave. The latter, according to the view put forward in this paper, ought to result in the magnetic birefringence curve also being concave, if the magnetic characters of the molecule remain unchanged in solution. From the anomaly observed here, we have, therefore, to suppose that in the case of nitrobenzene the magnetic characters of the molecule also are affected by mixing it with another component, besides the optical characters. Such an assumption is not quite out of place as nitrobenzene is ordinarily an associated liquid.

6. Summary.

The two outstanding features which Chinchalkar and other workers have observed in the study of the magnetic birefringence of liquid mixtures have been explained for the first time quantitatively by introducing the

new idea of a varying set of anisotropic polarisation field coefficients. The actual variations which the coefficients undergo with changing concentration have been determined from the observed refractivities of mixtures of the requisite composition. Although only typical mixtures have been dealt with in detail in the course of this paper, it may be remarked that the general conclusions hold good in all the mixtures so far studied.

The author is highly thankful to Mr. S. Bhagavantam, for his interest in the work and to the Syndicate of the Andhra University for its continued financial support to the author.

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ABSORPTION SPECTRA OF TETRA-ALKYL AMMONIUM SALTS.

(Contributions to the Theory of Co-ordinate Linkage IX.¹)

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Introduction

It is well known, that the conventional theory of valency as developed by Lowry, Sidgwick, and co.² assumes that only certain configurations of shared electrons confer stability to a molecule. The stability of the electron octet, emphasised in analogy with the configuration of the heavier rare gases by Langmuir, was the starting point of this theory, and later on also other configurations of 12 and 16 shared electrons have been admitted. Consequently it was assumed, that molecules which do not follow this generalised octet rule, possess different kinds of non-electrovalent linkage. Thus, in the nitro-compound the two bonds in the NO_2 group shall be different and only one of them shall be true covalent bond. These considerations find their brief formulation in Sidgwick's covalency rule, which postulates the maximum number of true covalent bonds to be 4 for the second short period (Li-F), 6 for the two following short periods and 8 for the heavier atoms. A number of arguments have been put forward against this conception and a theory which ascribes chemical stability to any molecule in which the sharing electrons form completed orbitals and the molecule as such is in a term of $^1\Sigma$ type is also possible.³ Whereas the first theory is a development of Lewis' octet rule, the second emphasises Lewis' pair-bond conception and follows more the ideas of Grimm and Sommerfeld.⁴ In such a theory the maximal number of (covalent or electrovalent) bonds always equals the number of outside electrons of the atom and different types of non-electrovalent bonds are not necessary. Thus nitrogen in nitro-compounds or in N_2O_5 is simply penta-covalent, because it possesses 5 valence electrons. The obvious differences of analogous atoms of the different periods find their explanation in energetical considerations. The non-existence of NCl_5 together with the existence of PCl_5 is then due to the

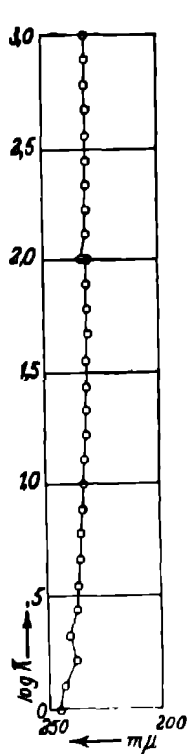


FIG. 1.

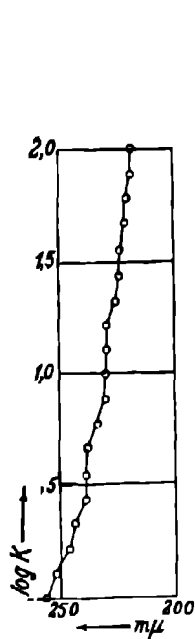


FIG. 2.

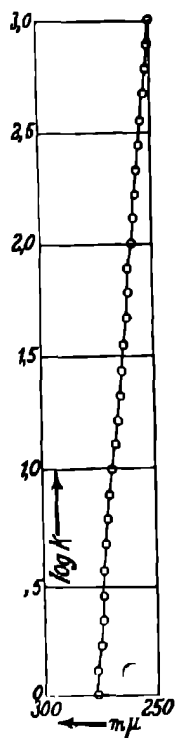


FIG. 3.

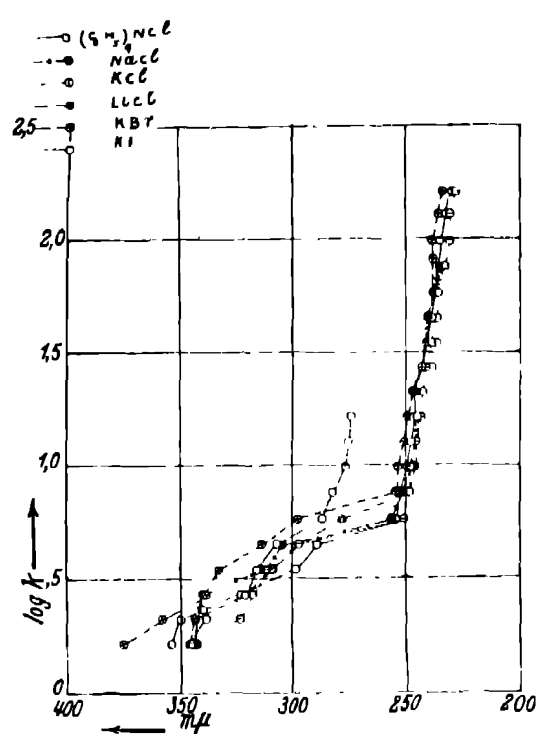


FIG. 4.

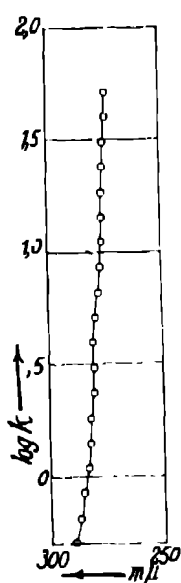


FIG. 5.

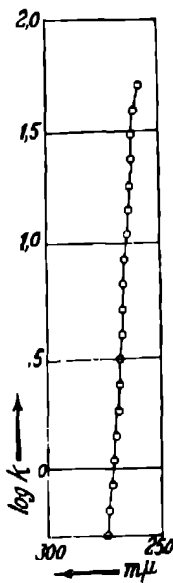


FIG. 6.

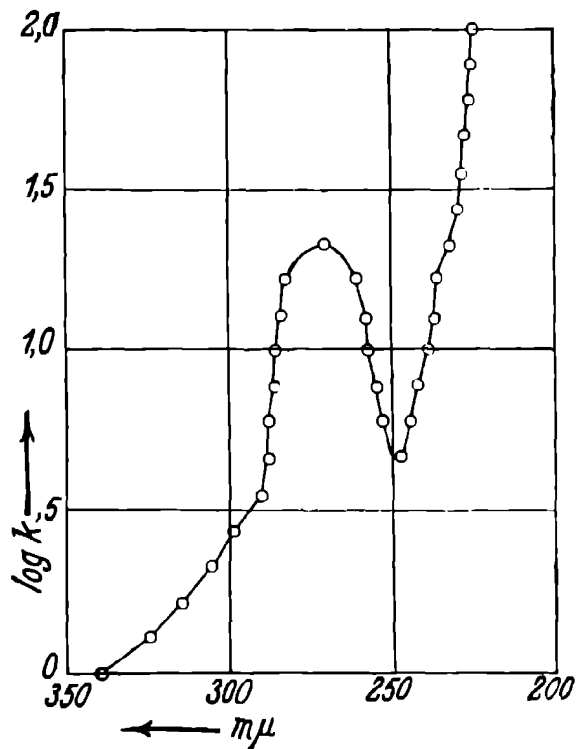
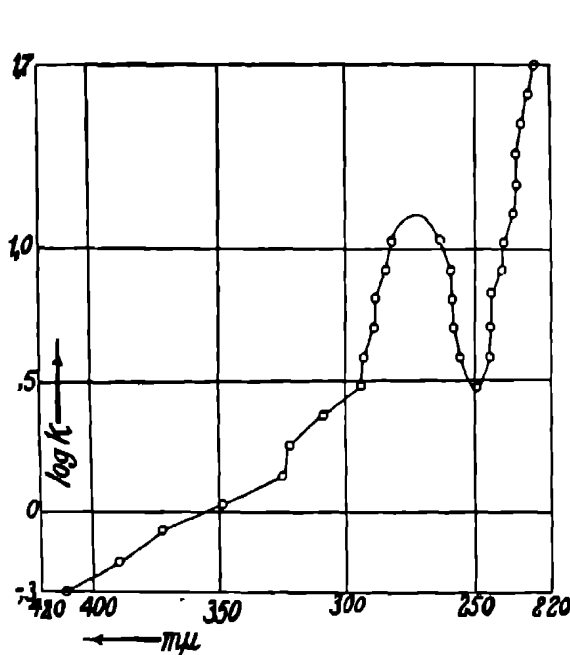
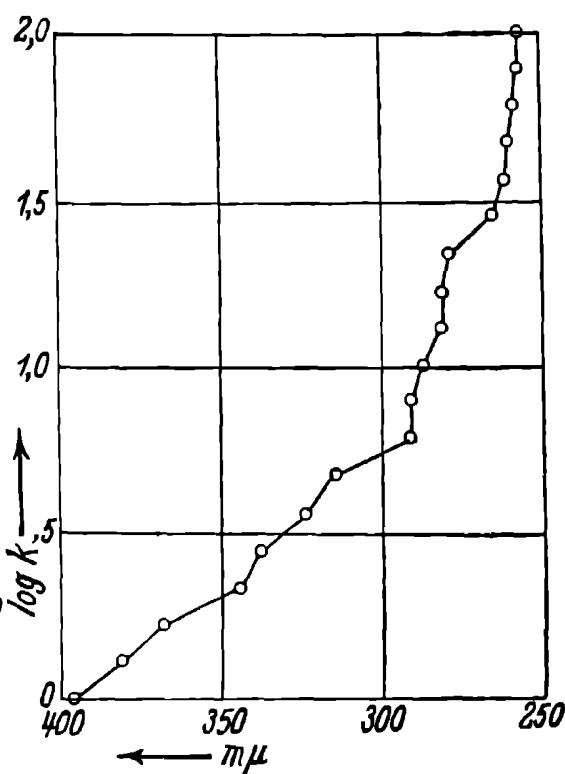


FIG. 7.

- FIG. 1. $(\text{CH}_3)_4\text{NCl}$.
 FIG. 2. $(\text{CH}_3)_4\text{NBr}$.
 FIG. 3. $(\text{CH}_3)_4\text{NI}$.
 FIG. 4. $(\text{C}_2\text{H}_5)_4\text{NCl}$ in different solvents.

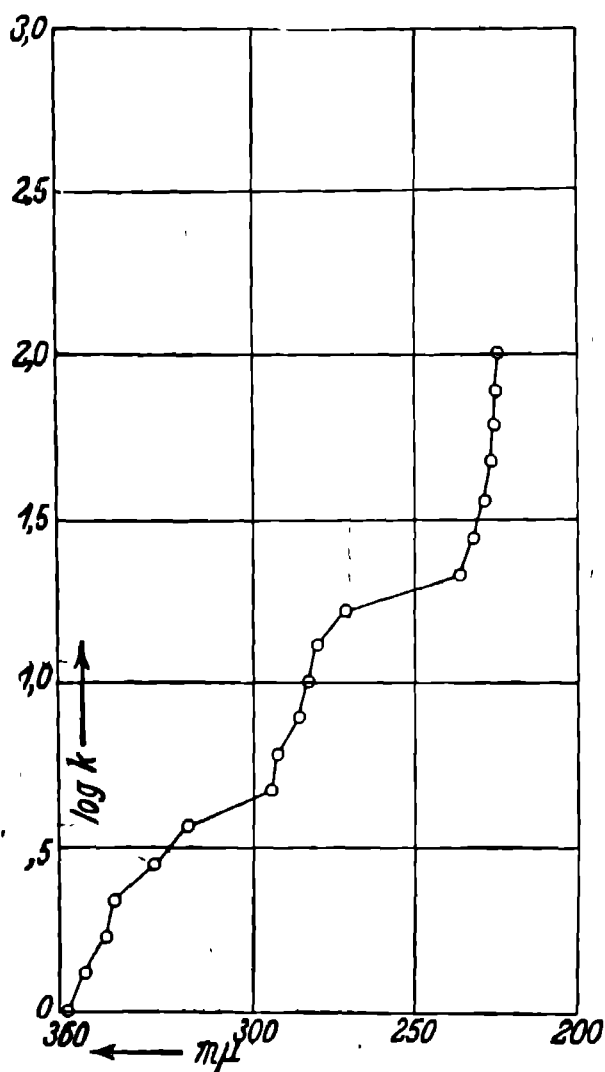
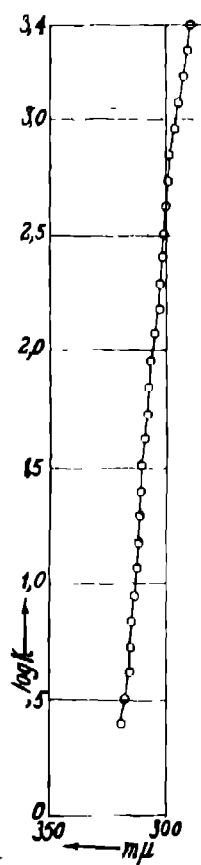
- FIG. 5. $(\text{C}_2\text{H}_5)_4\text{NBr}$.
 FIG. 6. $(\text{C}_2\text{H}_5)_4\text{NI}$.
 FIG. 7. $(\text{C}_3\text{H}_7)_4\text{NCl}$.

higher energy of excitation necessary to split the s^2 group of electrons of the nitrogen atom. It should be mentioned in this connection, that during the preparation of various nitrogen fluorides Ruff and his collaborators⁵ have found quite definite evidence of the existence of NF_5 . Sometime ago Ebert and Lange⁶ in the course of cryoscopical measurements found certain deviations from the behaviour, expected by the Debye-Hueckel theory in the case of strong solutions of certain tetra-alkyl ammonium halides, which clearly show, that some of these salts do not dissociate completely in water. The effect becomes more marked with the increase in mass of the organic

FIG. 8. $(\text{C}_3\text{H}_7)_4 \text{NBr}$.FIG. 9. $(\text{C}_3\text{H}_7)_4 \text{NI}$.

radical and the substitution of halogens possessing lower electronic affinity. These measurements, however, are not qualified to distinguish between the non-dissociated molecules with a true covalent nitrogen-halogen bond, and pairs of ions, *i.e.*, non-dissociated but still electrovalent molecules kept together by electrostatic forces, or the effect of formation of association of the ions themselves or of ions and water molecules. For the theories of valency, however, it would be of great interest indeed, to find out, if in solutions of tetra-alkyl ammonium halides there is really an equilibrium between electrovalent and covalent molecules, because it would contradict

the first and confirm the second of the above theories. Even if the percentage of covalent molecules is small, the existence of molecules in which nitrogen possesses five single covalent links would be of interest. Ebert and Lange emphasise, however, that it will not be possible to interpret their results by the introduction of one kind of interaction only and therefore it could be hoped for, that investigations of the absorption spectra

FIG. 10 $(C_4H_9)_4 NBr$ FIG. 11 $(C_4H_9)_4 NI$

may contribute at the same time to the question of the structure of highly concentrated solutions of electrolytes in water. From these points of view we have undertaken an investigation of the absorption spectra of these salts in solutions of high concentrations ($c = 1.0$ to $0.1 m$) as well as in those of low concentrations ($c = 0.01$ to $0.00001 m$).

Solutions of High Concentration.

For the measurements of the absorption spectra we employed at first a method, used in this laboratory and, besides later minor improvements, originally described elsewhere.⁷ As in many other similar methods, twin spectra of the solution and (with reduced illumination) of the solvent are taken with different concentrations and absorbing layers, and the wavelengths of equal intensity observed visually. The introduction of a discharge tube with stagnant gas, giving the continuous hydrogen spectrum,

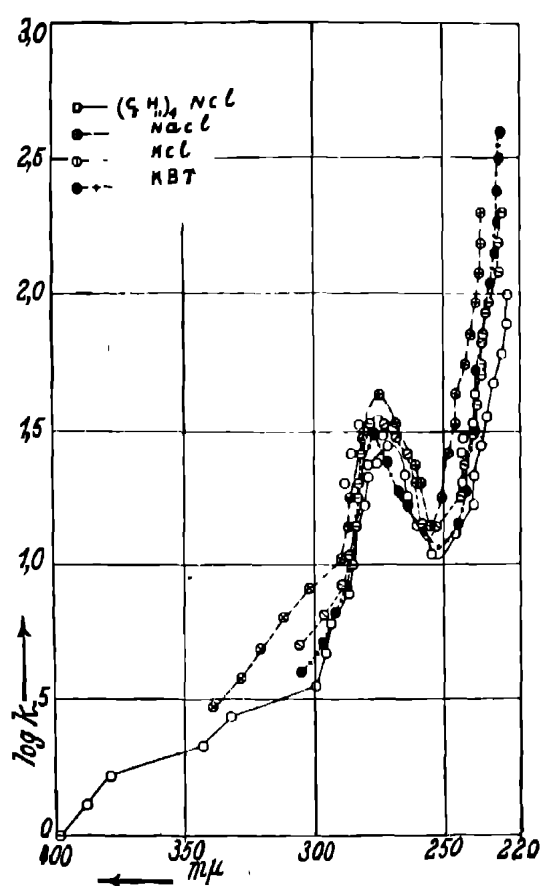


FIG 12

FIG. 12. $(C_5H_{11})_4 NCl$ (iso) in different solvents.

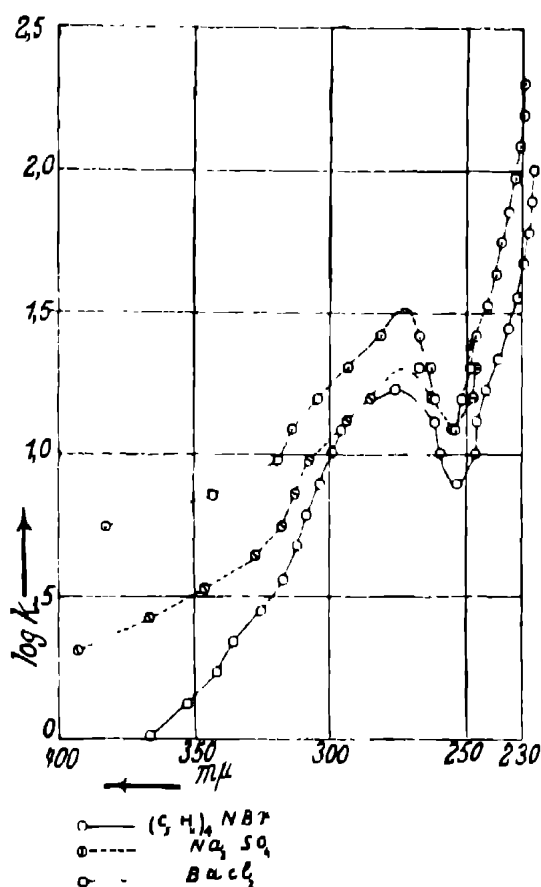


FIG 13.

FIG. 13. $(C_5H_{11})_4 NBr$ (iso) in different solvents

makes certain simplifications possible. The results, obtained with this method, indicated certain deviations from Beer-Lambert law and have been supplemented by precision measurements, in which the intensities of twin spectra of solution and solvent with equal illumination were directly measured by means of a recording microphotometer.

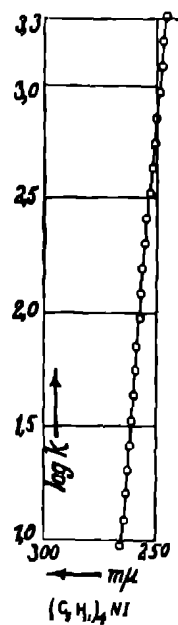


FIG. 14

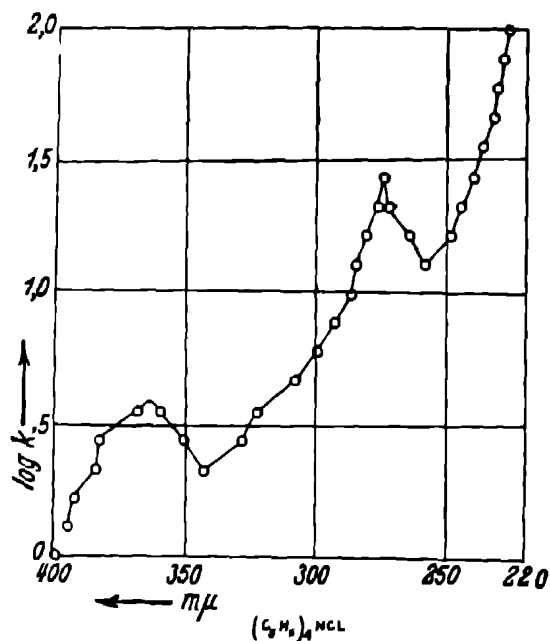


FIG. 15.

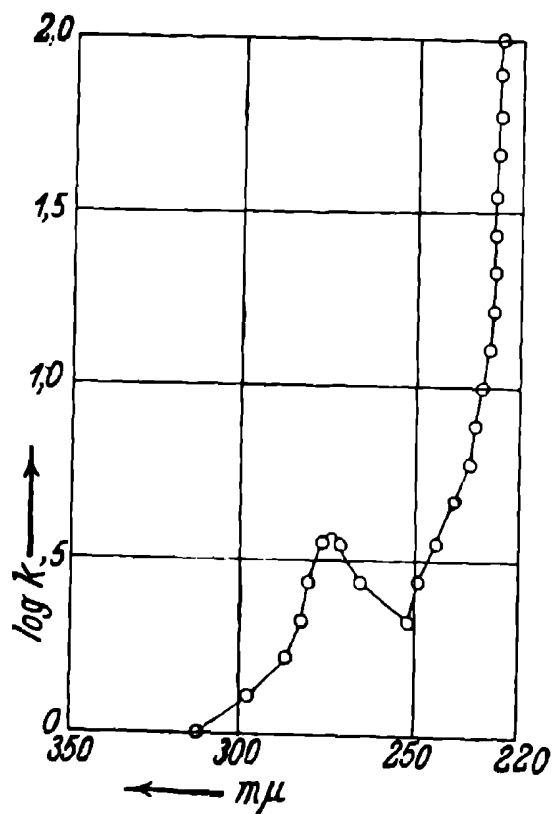


FIG. 16.

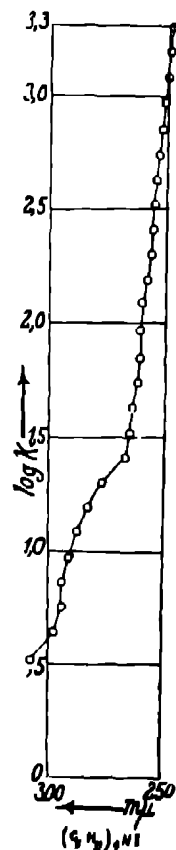


FIG. 17.

FIG. 14. $(C_5H_{11})_4NI$ (iso).FIG. 15. $(C_5H_{11})_4NCl$ (Normal).FIG. 16. $(C_5H_{11})_4NBr$ (Normal).FIG. 17. $(C_5H_{11})_4NI$ (Normal).

The results of the first series are given in the diagrams of figures 1 to 17. Here the absorption coefficient k is defined by the equation $I = I_0 \cdot 10^{-kcd}$, I_0 and I being the intensities of light, entering the medium and emerging from it, c and d stand for the concentration of the solution and the thickness of the layer. The concentration of these solutions was of the order 1.0 to 0.1 m . The absorption curves are shown in figures 1 to 17.

TABLE I.
Maxima of Salts R_4NX .

R =	Chloride		Bromide		Iodide	
	Ist Max $\lambda (m\mu) \log K$	II Max. $\lambda (m\mu) \log K$	Ist Max. $\lambda (m\mu) \log K$	II Max $\lambda (m\mu) \log K$	Ist Max $\lambda (m\mu) \log K$	II Max. $\lambda (m\mu) \log K$
CH_3
Max. conc	1 m		0.1 m		0.2 m	
C_2H_5	diffuse	diffuse
Max. conc.	0.2 m		0.2 m		0.2 m	
C_3H_7		270 1.3	~320 0.25	270 1.1	~315 ~0.6	~280 ~1.1
Max. conc.	0.1 m		0.2 m		0.1 m	
$n-C_4H_9$			320 0.55	270 1.2		
Max. conc.			0.1 m			
$n-C_5H_{11}$	364 0.55	274 1.4		274 0.6		~270 ~0.4
Max. conc.	0.1 m			0.1 m	0.005 m	
$i-C_5H_{11}$	~360 0.35	272 1.4	~330 0.15	277 1.2
Max. conc.	0.1 m		0.1 m		0.005 m	

From the comparison of the curves it will be seen that from $R=C_3H_7$ onwards selective absorption obtains. Mostly we have one well-defined and sharp maximum at about 270 $m\mu$ and another, more diffuse one preceding it at about 310 $m\mu$. The first one is always sharp. In $(C_4H_9)_4NI$ it is apparently only superimposed on the ascent of the band which is exhibited by the iodine ion at 227 $m\mu$. For such diffuse maxima we have taken the turning points of the curves as maxima and have deducted the probable value of the short wave ascent from its k value. The results are

summarised in Table I. It is interesting to note, that in general the selective maxima occur with heavier radicals, but in each series the chloride appears to develop them stronger than the bromide or iodide. In $(C_8H_{11})_4 NCl$, *i.e.*, the heaviest of the chlorides, the maximum at $310\text{ m}\mu$ is just indicated, but a further maximum at about $365\text{ m}\mu$ is developed, which could not be found in the other curves. This latter one appears quite distinct in the *n*-molecule and is still indicated in the iso-compound. In the series with $R = C_7H_5$, the chloride shows already indications of the maxima, even if only diffuse and at low values of $\log k$, the bromide and iodide show a continuous end absorption only, like the salts with $R = CH_3$. In the series with $R = C_3H_7$ we find a slight decrease of the $\log k$ values in the same directions, which is more strongly marked in the series with $R = n - C_8H_{11}$, where the $\log k$ values of the main maximum at $274\text{ m}\mu$ decreases from 1.4 in the chloride to 0.6 in the bromide. The corresponding figures for the iso-forms are 1.4 for Cl, and 1.2 for Br.

Since the main maximum possesses about the same wave-length independent of X being Cl, Br or I, it seems reasonable to assume, that this selective absorption belongs essentially to hydrated R_4N^+ ions. On the other hand, the maxima appear only with heavier radicals, and it contradicts every experience to assume that the selective absorption if it belongs to the C — N link, should obtain only when longer chains are attached to the C atom. Furthermore, if this absorption would be due to the R_4N^+ ions alone, the differences in intensity ($\log k$) values between chlorides, bromides and iodides and those between the normal and iso forms of $(C_8H_{11}) NBr$ and $(C_8H_{11}) NI$ could not be explained.

Further corroboration is furnished by the optical behaviour of these salts in the presence of foreign salts. The solution of $(C_2H_5)_4 NCl$, where the maxima are still found indistinct at low values of k , shows, that all curves in the presence of foreign ions are shifted in the same sense against the curve in water; only the absorption coefficient is increased and the curves are slightly shifted towards red. Those in solutions of the three chlorides LiCl, NaCl, and KCl are close together, while those in solutions of KBr and KI show stronger effects. (Cf. Fig. 4.)

We have then measured solutions of $(C_8H_{11})_4 NCl$, where the maximum is more distinct than in the former ones, in the presence of NaCl, KCl, and KBr and of $(C_8H_{11})_4 NBr$ in the presence of Na_2SO_4 and $BaCl_2$. It can be seen (Figs 12 and 13) that again the curves of the former salt in solutions of NaCl and KCl are close together, whereas the $\log k$ value reaches appreciably higher values and the curve broadens in the presence of the Br ion. Here the influence of the negative ion is clear. The changes of the

absorption coefficient to our mind are more important than those of wave-length. Table II gives the wave-lengths in $m\mu$ of the maxima obtained.

TABLE II.

Chloride		Bromide	
In water	272	In water	277
In water + NaCl	276	In water + Na ₂ SO ₄	275
In water + KCl	275.5	In water + BaCl ₂	275
In water + KBr	275		

It does not appear to us to be impossible that the differences of wave-length are below the sensitivity of the experimental method and that these experiments do not allow us to distinguish accurately between the wave-length of the maxima in the presence of foreign ions. We cannot be certain whether the differences between 276 and 275 $m\mu$ are real. It can be seen, however, that the maximum of the bromide, compared with that of the chloride, in water without additional salts, is certainly shifted towards red and that, independent of this, the maximum obtains a position at about 275 to 276 $m\mu$ in the presence of foreign salts.

*Some Remarks on Optical Effects in Concentrated Solutions
of Strong Electrolytes.*

The interpretation of these effects leads us to the question of the structure of solutions of strong electrolytes at higher concentrations. It is well known, that the theory of Debye-Hueckel still needs further development to explain the behaviour of such highly concentrated solutions, c being about 1 to 0.01 m . From the point of view of the optical behaviour of strong electrolytes and particularly as regards absorption spectra the problems connected with this question have been discussed by Scheibe⁸, von Halban,⁹ and Fromherz,¹⁰ and their collaborators. Scheibe and Fromherz interpret the observed changes in the selective absorption of various ions due to the presence of foreign salts, in terms of changes in the deformation of the absorbing ions in the unlike field of the anti-ions, which may form a surrounding atmosphere of opposite charge or may form pairs with the absorbing ions according to the conceptions put forward by Bjerrum¹¹ to adapt the Debye-Hueckel theory of strong electrolytes to higher concentrations. Von Halban and his collaborators have on the other hand always

maintained that other influences exist too and in the last paper of Kortuem¹² not the interaction between oppositely charged ions but the effects of hydration and dehydration, or, in other words, the interaction of the absorbing ion with the dipole molecules of the solvent are held mainly responsible for the observed changes of the absorption curve.

To our mind it is evident, that both effects play a rôle and that the observed changes as for instance those of the absorption of $R_4 N^+$ ions above cannot be expressed in terms of one parameter only. A simple reference to the properties (hydration, polarisability, or diameter) of the anti-ions alone is not sufficient and the influence of the ions of like charge is certainly present here as well as in other instances as shown in previous papers of this series. We have mentioned above that also Ebert and Lange⁶ have come to a similar conclusion from cryoscopical measurements and a number of authors have already emphasised that the structure of solutions of electrolytes at higher concentrations is rather a complex phenomenon. Special mention may be made of the measurements of Darmois¹³ on the optical activity of tartrates in the presence of neutral salts, which have led him to the assumption, that dehydration and deformation influence the optical activity in the opposite way.

But the conclusion that the interaction effects in higher concentrated solutions of strong electrolytes are of a complicated nature and that various different effects exist side by side, is about the only one which in the present moment can be made with certainty. How difficult it is, to predict the result of any one of the various possible effects, say of hydration or deformation of the absorbing ion, on its selective absorption, will be seen, when the Franck-Condon diagram which has already served as a useful instrument in so many discussions on the absorption and emission of isolated molecules in the vapour state, is made the basis of discussion.

The three-dimensional Franck-Condon diagram of a molecule $A^+(BC)^-$ — we may think of KOH—may be represented schematically in a simplified manner in Fig. 18. The ground level of the ion $(BC)^-$ may be formed by the union of $B + C^-$ and the level of these separated constituents $A^+ + B + C^-$ will be above that of the neutral atoms $A + B + C$, since generally the electronic affinity of C will be smaller than the ionisation potential of A. In any case we will find, in analogy to diatomic and polyatomic molecules in the vapour states, a number of repulsive curves and an absorption of light, *i.e.*, a transition from the ground level to any one of them, will produce a region of continuous selective absorption which may be correlated to a process of photo-dissociation or to the tearing off of the superfluous electron of the negative ion in solution, the latter spectra may also be due to the

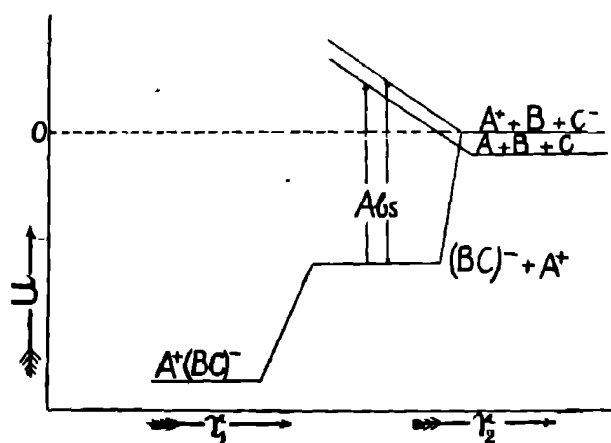


FIG 18. Scheme K of Franck-Condon Diagram of a Triatomic Salt

transition of the electron to a molecule of the solvent under formation of *e.g.*, OH^- ions as shown by Franck and Haber¹⁴ but such complication shall not be considered here. It is, however, evident, that the absorption of light is represented by the upper part of the energy diagram, which belongs essentially to the $(\text{BC})^-$ ions, representing its dissociation or formation, in which the A^+ ion does not take any part, but is considered to be at infinite distance, in the level of the separated constituents $\text{B} + \text{C}^-$ as well as in that of the ground level of the ion $(\text{BC})^-$. The formation of $\text{A}^+(\text{BC})^-$ originates from the latter one and is represented in the lower part of the diagram. If we consider now those conceptions which assume in higher concentrated solutions the formation of associations of the A^+ and the $(\text{BC})^-$ ions, either as atmospheres of oppositely charged ions or particularly as pairs of unlike ions, this will be a process in which A^+ ions are not any longer at an infinite distance from the $(\text{BC})^-$ ions and which is therefore connected with this lower part of the energy diagram. Any change due to deformation of the ion $(\text{BC})^-$ in its unexcited level will therefore have quite different effects on the two parts of the diagram, since this level forms the lower state for the representation of the selective absorption and the upper one for the formation of undissociated ions $\text{A}^+(\text{BC})^-$. According to Kortuem's measurements the absorption spectrum of dinitrophenol does not undergo any change in concentrations of medium strength (up to 0.01 *m*) in which activity coefficients, conductivity and similar observations indicate already deviations from the theory of Debye-Hueckel. For still higher concentrations he finds changes of the optical properties, but these do not go parallel with those formed by means of thermodynamical and electrochemical measurements. He concludes that the interaction of the absorbing ion with the molecules of the solvent is the essential effect, and not that between the ions of opposite charge. From the above diagram it is evident, that this

is by no means conclusive for the reason, that absorption and approach of unlike ions belong to quite different parts of the energy diagram.

In Fig. 19a the lower part of this diagram has been used to represent the process of hydration of the system $A^+ (BC)^-$. In the process of hydration or solvation a certain amount of energy is liberated, which has to be added for all internuclear distances and brings about a lower position of

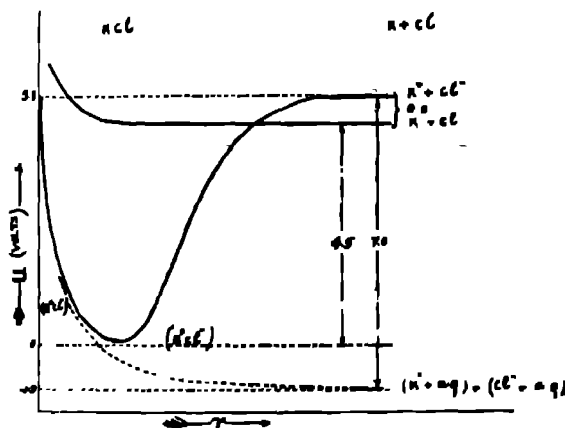


FIG. 19a. Franck-Condon Diagram of a Triatomic Salt 1st Part.

the $U : r$ curve. If the undissociated molecule is an electrovalent one* the hydration energy of the two ions together represents naturally a much bigger amount than that of the undissociated molecule because the number of water molecules held by the two separate ions and the force by which they are bound to them is much larger than for the neutralised molecule itself. This is evident for those simpler diatomic salts for which all figures, *i.e.*, ionisation potential, electronic affinity and energy of hydration of the two ions and the heat of formation of the gaseous compound are known; Potassium chloride may serve as an example¹⁵ and its Franck-Condon diagram is given in figure 19b. In KCl the level of the separated ions is about half a volt above that of the separated neutral and unexcited atoms. The energy of hydration is known to be 73 k.cal./mol. for K^+ and 89 k.cal./mol. for Cl^- and hence the level of the separated ions in the state of hydration lies about 7 volts below that of the unhydrated ones or about 6.5 volts below that of the separated neutral atoms. The ground level of the undissociated gaseous ionic molecule (K^+Cl^-) lies about 103 k.cal. or 4.5 volts below that of the neutral atoms or still about 2 volts above that of the hydrated ions and the energy of hydration for this form will be very small,

* The term electrovalent is used, when the adiabatic excitation of the vibrational levels of the ground state dissociates a molecule into ions, and a molecule is called covalent, when the adiabatic dissociation of its ground state involves neutral atoms.

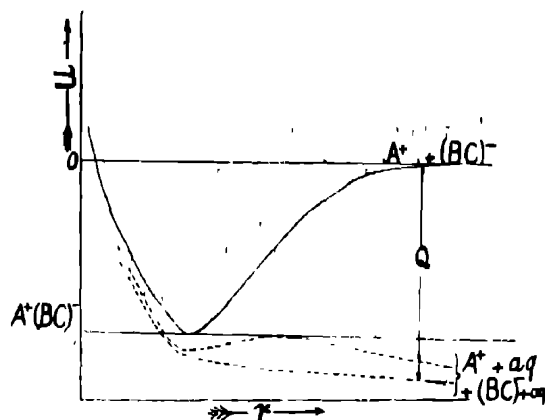


FIG. 19b. Franck-Condon Diagram of KCl

because the opposite charges cancel each other. The fact, that KCl dissociates in aqueous solutions shows already that the hydration energy of the undissociated molecule is less than this difference of about 40 k. cal./mol. and that the level of the separated hydrated ions has become the lowest one of the system. The great difference of the hydration energy of the two systems $K^+ + Cl^-$ and $(K^+Cl)^-$ turns the $U : r$ curve into a repulsive one and as a matter of fact the above is only a description of the process of hydrolytic dissociation by means of the Franck-Condon diagram. Similar repulsive curves have to be expected quite generally for molecules dissociating into ions and even if the electrovalent curve of the non-hydrated molecule is not that of the ground level but near to it, that involving the separated hydrated ions may intersect the potential curve of the ground level and may become the lowest one of the system,¹⁴ as in AgCl.

Two conclusions become evident at once from this description by means of the $U : r$ curves. In Fig. 19a the lowest dotted curve represents the dissociation process due to the difference of hydration energy and is shown here as a repulsive curve. If, however, the concentration is increased and the number of water molecules at the disposal of the individual molecule $A^+(BC)^-$ is appreciably decreased, the energy of hydration decreases too, and the original curve of the gaseous state being the limiting case in which the hydration energy vanishes, higher curves of the hydrated system should be expected, showing a labile minimum in the neighbourhood of the internuclear distance of the gaseous molecule. An attempt to draw such a curve is shown by the upper dotted curve of Fig 19 a, but in any case such curves with a slight minimum must come into existence if the additional energy of hydration is sufficiently decreased. Such a minimum may be taken as the energetical representation of Bjerrum's pairs of ions.

Secondly, this diagram of the position of the electronic terms of the system $A^+(BC)^-$, depending on r , does not give any indication as to the change of the selective absorption of the ion $(BC)^-$. In this description r represents the distance between the cation and the (BC) anion, the latter one is taken as an entity and the change of the relative position of its own electronic terms, on which its optical properties depend, does not appear at all, and has no direct connection with the dissociation process of the cation and the anion. Hence one set of observations like electrical conductivity, concerning the system $A^+ + (BC)^-$, may well indicate the existence of non-dissociated ions in such concentrations, in which absorption measurements show that the relative position of the terms of the $(BC)^-$ ion itself has not yet changed

The change of wave-length as produced by the addition of hydration energy to the system depends again on whether the hydration of the undissociated ion $(BC)^-$ or that of the separated system $B + C^-$ is the greater. Fig. 20 represents the case in which the separated system $B + C^-$ gains more energy than the complex ion $(BC)^-$. The change in wave-length pro-

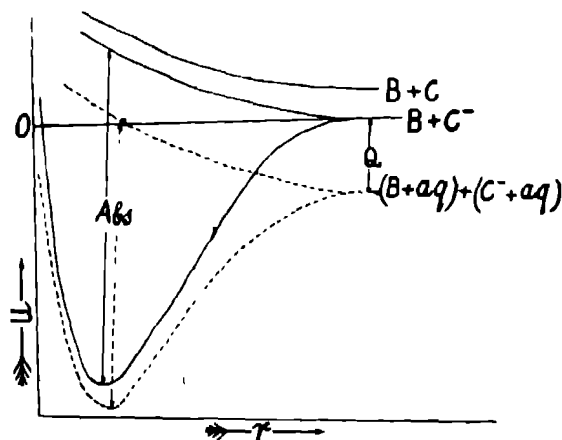


FIG. 20 Franck-Condon Diagram of Triatomic Salt. 2nd Part

duced in this way is always a small effect and we may therefore assume that the general form of the potential curve remains unchanged and that excited states become less and less affected. If then the energy difference between the unhydrated system (full lines) and the hydrated one (broken lines) is bigger on the right-hand side for the separated constituents than on the left-hand side for the completed ion, the effect of such an increase of energy will be to shift the region of selective absorption slightly towards red, and the dehydrating effect of the presence of ions of like or unlike charge in the solution will shift the maximum towards shorter wave-length. This effect seems to exist in certain of Warner's complex salts, investigated

earlier,¹ *e.g.*, when the absorption curves of $\text{Na}_3[\text{RhCl}_6]$ does not differ, in the presence of NaCl and KCl but is shifted towards the ultra-violet when the additional salt is replaced by Na_2SO_4 . Indeed it is very plausible to assume that the hydration energy of such a complex ion is less than the sum of those of its constituent ions and the characteristic influence of the ions of like charge can be explained in this way quite well. When, however, the hydration energy gained by the separated system happens to be smaller than that of the united ion, just the reverse effect has to be expected, and in cases like the R_4N^+ ions it is not easy to decide, which hydration energy may be the larger one. It could be argued that the field in the neighbourhood of a completed ion will always be smaller because the charge is the same as in the separated constituents, while the radius is bigger. But this will not be true always; the charge is not evenly distributed but localised in the molecule and new dipole moments may be produced in the N — R bonds. More often, however, the hydration energy of the separated system should be bigger and therefore hydration should produce a shift towards longer, and dehydration by the neutral salts added to an aqueous solution, towards shorter wave-lengths. Such considerations seem to explain also most of the effects observed on the absorption curves of organic molecules in different solvents.

Superimposed on this effect is that of the deformation of the absorbing ion by the field of an added foreign ion. Whereas the first effect may be produced by ions as well of like and of unlike charge, this second effect may be expected to be characteristic for the ion of opposite charge, because such ions will be found in the neighbourhood of the absorbing ion or will pair with it at stronger concentrations. Not very much can be said about the result of such a deformation on the absorption itself. In the Franck-Condon diagram such an effect will produce a change in the internuclear distance of the minimum position and, furthermore, the energy of dissociation and the whole force system and the slope of the curves will be changed. In this connection, however, the rule of Fajans and Joos¹⁶ may be mentioned, according to which the electronic configuration of a cation will be loosened while that of the anion consolidated by the mutual deforming influence. This rule has been confirmed by many observations on monoatomic ions. We will assume that it holds also for more complex ions, because at least for the anions there should not be much difference. This is not so certain for cations, because the complex cations possess outside electrons, which the monoatomic ones mostly have lost. We remember again, that the effects in question are only slight, and we assume therefore that the changes on the potential curves are slight too and may be neglected increasingly

for the higher terms. In this case we expect that the absorption maximum of a cation will be shifted towards longer wave-lengths, that of an anion towards shorter wave-lengths as a result of the deforming influence of an ion of opposite charge. In the Franck-Condon diagram, the consolidation of the electronic configuration may be compared to the normal case of band spectroscopy in which the ground level possesses a smaller τ , larger vibrational frequency and larger energy of dissociation than the excited level and the loosening of the electronic structure to the reverse, normal case. The ground level corresponds to the ground level of the undeformed, the excited to the ground state of the deformed molecule. If the repulsive curve does not suffer more than very slight changes, the energy difference between that and the ground level will be decreased in the former and increased in the latter case. Such a conception appears well qualified to explain many effects observed on the absorption curves of inorganic ions and is more or less identical with certain conceptions, developed by Scheibe and his collaborators.

There is, however, still another effect possible already discussed by Fromherz. These two cases of deformation, essentially a decrease or increase of the polarisability, may effect mainly the absorption coefficient and not the wave-length. According to the theory of dispersion the polarisability is directly proportional to the absorption coefficient and inversely proportional to the frequency, and anions in the field of deforming cations can then show a decrease in the absorption coefficient, cations in the field of deforming anions an increase.

We have seen, that the selective absorption of the tetra-alkyl ammonium salts appears gradually with increasing weight of the radical and is not identical in *n* and *i* forms. This effect appears to be due to the deformation of the ion in the field of the hydrating water molecules, which is different according to the size and arrangement of the radical and therefore we have ascribed the selective absorption to the hydrated ions. The dehydrating effect of Cl^- is bigger than that of Br^- and consequently the larger deformation in $(\text{C}_8\text{H}_{17})_4\text{NBr}$ produces a maximum at a slightly longer wave-length than in $(\text{C}_8\text{H}_{17})_4\text{NCl}$. At the same time there is a marked difference of intensity between chlorides, bromides, and iodides, the *k* values of the chlorides being the greater one. This effect cannot be ascribed to the dehydrating influence of the anion as the Cl^- ion is the more hydrated and hence the more dehydrating one, and this effect has to be interpreted as a true deformation of the cation by the anion. These absorptions concern mainly, but not entirely, the value of the absorption coefficient and come therefore under the last of the above headings. But

it is clear, that both effects, the interaction with the molecules of the solvent and with the oppositely charged ions have to be considered.

This is corroborated by the optical effects, produced by foreign ions. All three curves of $(C_8H_{11})_4 NCl$, in the presence of NaCl, KCl and KBr lie at longer wave-lengths than that in water only, the KCl and NaCl curve closer together, that in a KBr solution more apart. This indicates the deforming influence of the anion on the cation and the effect of the Br^- ion is probably slightly the stronger because the radius of the hydrated Br^- ion is smaller than that of the hydrated Cl^- ion and it can approach the cation more closely. Again the dehydrating effect of the positive ion can be seen from the curve of the bromide in a solution of $BaCl_2$, which is much above that in Na_2SO_4 , but only as far as the absorption coefficient is concerned.

The curves of $(C_2H_5)_4 NCl$ in the presence of foreign salts show exactly the same behaviour. On account of the deforming influence of the anion on the R_4N^+ ion, all curves are slightly shifted towards the red and have increased k values. Those due to the Cl^- ion are all closer together, than the other ones, the effect being more marked in the order $Cl^- < Br^- < I^-$, *i.e.*, in the order in which the radius of the hydrated halogen ions decreases and the minimum distance of approach therefore decreases too.

These few remarks will be sufficient to show, that the effect of both kinds of interaction have to be considered and that the long wave-length maxima are due to the hydrated R_4N^+ ions

Measurements on the Absorption Band of the Iodine Ion, at Low Concentrations

Further experiments concern such solutions of low concentrations for which Beer's Law has been found to be rigorously valid in many cases and particularly for the bands of the iodine ion. This gives us an opportunity to ascertain whether there exist indications of a true covalent nitrogen-halogen bond. This was done by a precision method, as mentioned above, since the percentage of such covalent molecules is necessarily very small. A sample microphotogram of two solutions of $(C_8H_{11})_4 NBr$, taken on the same plate together with that of the source of light through distilled water only is shown in Fig. 21, Plate XXII. In each case the exposure time is exactly equal, the one solution, however, has a strength of $\frac{M}{10}$ in an absorption cell of 9.99 mm. length, whereas the other solution had a strength of $\frac{m}{100}$ and the length h of the absorption cell was 99.983 mm. It can be seen, that the absorption curves join exactly on the long wave side, showing that the

illumination was indeed identical and no errors due to slight changes in the adjustment have occurred. In the region of the selective absorption itself, however, the curve of the more concentrated solution lies definitely slightly below that of the more diluted one. In spite of the same number of molecules being present the number of absorbing centres has decreased, indicating that the number of association complexes, formed by the R_4N^+ ion, decreases with increasing concentration

From the discussion above, it is obvious that different interpretations of these maxima between 300 and 270 $m\mu$ are possible, and therefore such deviations from Beer's Law even without shift of wave-length are not conclusive for the existence of a true covalent bond. They may be taken as indicating the existence of still another form of association, but they do not give a definite answer as to the nature of such a second not dissociated form. There is, however, another possibility definitely to test whether this second associated form really is identical with a molecule, which possesses a covalent nitrogen-halogen bond covalent. Scheibe⁸ has found two bands belonging to the iodine ion, with maxima at about 226 and 192 $m\mu$. There is no doubt, that these two bands belong to the negatively charged iodine ion; the energetical difference of 7900 cm^{-1} of the two bands agrees with the doublet separation of the 2P ground level of the iodine atom of 7600 cm^{-1} and these two regions of absorption have been correlated to photo-dissociation processes $I^- + h\nu = e + I(^2P_{3/2})$ and $I^- + h\nu = e + I(^2P_{1/2})$ and it is probable that the electron forms OH ions subsequently. Fig. 22 shows the first of these two bands in a solution of concentration of $(CH_3)_4NI$. The photometer curve indicates that the absorption of the iodine ion persists in solutions of tetra-alkyl ammonium iodides. Its maximum was measured at 227 $m\mu$.

We have then compared the absorption of different concentrations. In order to increase the accuracy of the photometric measurements the exposure time was arranged in such a way, that all plates were not too dark but the spectra were just slightly grey; accordingly the maxima themselves are not very pronounced on these records. Fig. 23 shows the absorption of two solutions of $(C_5H_{11})NI$, firstly with $= \frac{m}{10,000}$ and $d = 10\text{ mm.}$, secondly with $= \frac{m}{2,000}$ and $d = 2\text{ mm.}$ Again the absorption curve of the more concentrated solution lies definitely below that of the more diluted one. In Fig. 24 the first of these two solutions is replaced by an even more diluted one, $= \frac{M}{1,00,000}$ and $d = 100\text{ mm.}$ it can be seen that the difference between the curves is still increased. Again the curves join exactly in the unabsorbed

region, showing that adjustment and illumination did not change. All curves have been taken from the same plate, to avoid possible differences of blackening due to developing. Similar results obtain also with lighter salts, *e.g.*, $(\text{CH}_3)_4\text{NI}$. The effect is certainly small and we do not intend to work it out quantitatively. But there is no doubt, that qualitatively the concentration of the iodine ion decreases with increasing concentration.

Scheibe and Fromherz and their collaborators have shown in a number of investigations, that for the maxima of the iodine ion at such low concentrations as used here, Beer's Law is rigorously valid. Moreover, at low concentrations from 0.001 onwards also other optical measurements of absorption spectra, refractive index, etc., as well as thermo-dynamical and electrochemical measurements have shown, that the properties of the ions are independent of concentrations. Furthermore, whenever with much higher concentrations a change of the k values of the bands of I^- has been observed it was accompanied by a change in wave-length, whereas in our measurements the wave-length of the maximum remains constant and the absorption coefficient alone is changed.

The optical constancy of these bands is very well known indeed and since the same amount of iodine was present in these solutions and since this particular band is characteristic for the negative iodine ion there appears to be only one possible interpretation, namely, that a certain percentage of iodine ions has lost its ionic character. This evidently means, that there exists still another form of the tetra-alkyl ammonium iodides, with which the dissociated molecules of the salt are in equilibrium, in which they possess a true covalent $\text{N}-\text{I}$ bond, and that nitrogen under favourable conditions can be penta-covalent in agreement with a pair-bond theory of valency.

The solutions of tetra-alkyl ammonium halides are apparently a mixture of three different forms. The bulk of a solution of R_4NX in water at low concentration is dissociated in R_4N^+ and X^- ions, as long as R is CH_3 or C_2H_5 . When R becomes heavier, association complexes are formed by the hydrated ions, in which also X plays a rôle (pairs of ions?), and the percentage of such complexes appears to be comparatively large at concentrations of 1 to 0.1 *m*. At the same time at least the iodides are in equilibrium with a small percentage of a third form which is characterised by a covalent bond between nitrogen and iodine.

In previous papers of this series^{1,17} we have already come to the conclusion, that the term 'complex salt' now-a-days is used for quite different classes of molecules. We have defined as "genuine complex salts" such compounds, in which the complex ion preserves its individual identity as such also in solution and in which physical measurements like absorption

spectra or Raman effect indicate some kind of true chemical, non-electrostatic linkage between the central ion and those molecules or ions which surround it. This definition excluded all cases of crystal water, or crystal alcohol, etc., where a definite co-ordination number is produced not by the number of co-ordinate bonds but by the geometrical properties of the crystal. It excludes furthermore cases like the hydrated ions of the transition elements, in which the absorption spectrum indicates that the water molecules are held as loose associations on account of electrostatic forces. It is interesting to note, that Day, Hughes, Ingold and Wilson¹⁸ on account of quite different observations have come to the same conclusion in the latter case.

But also in the class of genuine complex salts the co-ordinate bond appears to be the representation of quite different physical mechanisms in various cases. The absorption spectra of tetra-alkyl ammonium salts do not show any phenomenon which could not be attributed to ordinary covalent bonds between carbon and nitrogen. On the contrary, the transition to covalency of the nitrogen-halogen bond, which was observed for a small percentage in low concentrations directly contradicts the conception of the co-ordinate bond as originally developed by Werner. The most simple and straightforward description of the mechanism of linkage appears to be to attribute 5 covalent bonds to the N atom on account of its 5 outside electrons $2s^2 2p^3$. It is clear that among the five bonds that between nitrogen and halogen will be much more polarised than the four nitrogen-carbon bonds, and hence this bond will be the one which becomes electrovalent under the influence of additional outside energies like that of hydration or of the crystal lattice. If this is so, the tetra-alkyl ammonium salts do not belong to the same class as for instance the hexa cyanides of Co, but have to be considered as simple derivatives of pentavalent nitrogen. To our mind this conclusion is strongly corroborated by the fact, that, according to their absorption spectra,¹⁹ also inorganic nitrates are covalently bound in the vapour state and exhibit an electrovalent bond only in solution. The different chemical behaviours of the fifth bond of nitrogen appear to find its explanation more by considerations of bond energies and polarisation than by the assumption of a special quality of this bond.

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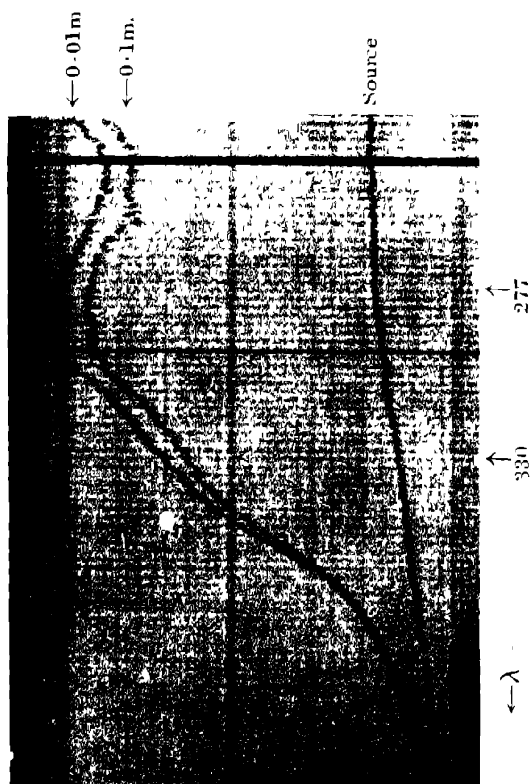


FIG. 21 Photom. Record, $(C_5H_{11})_3NI$

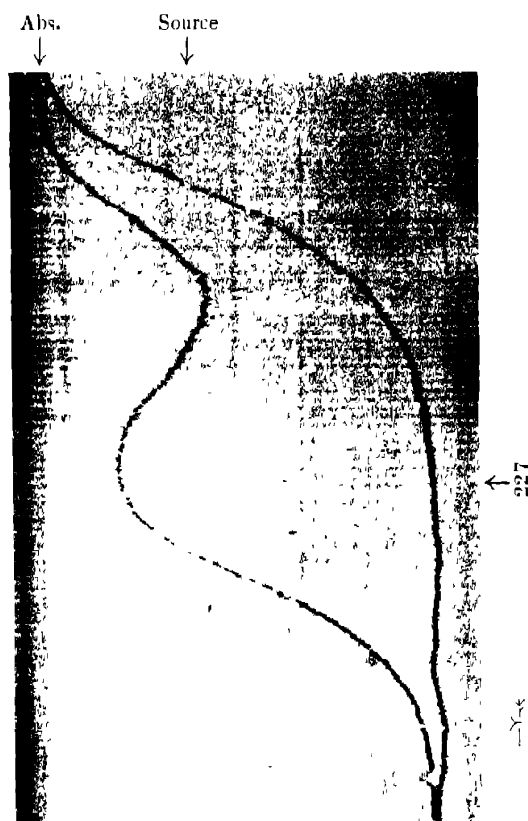


FIG. 22 Photom. Record, $(C_5H_{11})_3NI$ absorption.

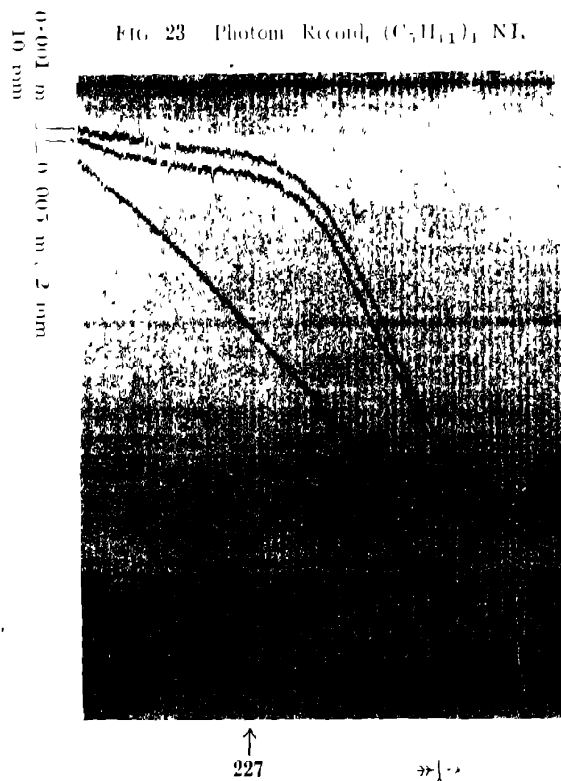


FIG. 23 Photom. Record, $(C_5H_{11})_3NI$

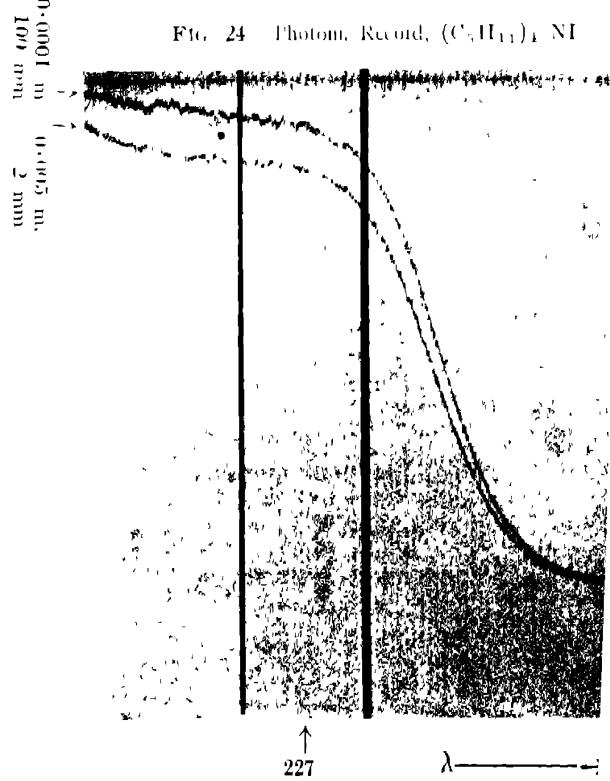


FIG. 24 Photom. Record, $(C_5H_{11})_3NI$

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EXPLANATION OF FIGURES IN THE PLATE.

- FIG. 21. Photometer record of $(C_5H_{11})_4 NBr$ solution. 0.1 m. and 9.99 mm, 0.01 m. and 99.98 mm.
- FIG. 22. Photometer record of $(CH_3)_4 NI$ solution.
- FIG. 23. Photometer record of $(C_5H_{11})_4 NI$ solution. 0.005 m. and 2 mm, 0.001 m. and 10 mm
- FIG. 24. Photometer record of $(C_5H_{11})_4 NI$ solution 0.005 m. and 2 mm., 0.0001 m. and 100 mm.

MAGNETIC SUSCEPTIBILITIES OF SOME ORGANIC COMPOUNDS IN DIFFERENT PHYSICAL STATES.

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1 Introduction

VAN VLECK¹ has shown that molecular susceptibility of a polyatomic molecule without a resultant spin can be represented as the sum of two terms.

$$\chi_m = - \frac{Le^2}{6mc^2} \sum r^2 + \frac{2}{3} L \sum \frac{|m_0(n' \cdot n)|^2}{h\nu(n' : n)}$$

The first term is the well-known Langevin term and the second is a paramagnetic term independent of temperature, arising from the distortion of the electron system due to the interatomic forces in the molecule. This paramagnetic term will vary with the state of the molecule. The magnitude of this term in the solid state, for example, will be different from the corresponding value in solution. When a salt is dissolved in a liquid, the binding forces in the solid state are destroyed, and the ions of the salt are surrounded by neighbouring solvent molecules which will also introduce some constraints.² In general therefore, we should expect a change in magnetic susceptibility when a salt is dissolved in solution (equal to the difference of the paramagnetic term in the two states). Several inorganic salts have been investigated by various workers and small changes of susceptibility observed in solution (on the average, about 2 to 3% increase in solution).³

No such work seems to have been undertaken in the case of organic compounds. Oxley⁴ has shown that several aromatic compounds suffer a change (roughly 5% in most cases) in diamagnetic susceptibility on melting. In most cases there was an increase in value; but in a few cases a decrease was also observed. Whatever might be the sign of the change, it is clear that this must be due to some fundamental change taking place in the transition from the solid to the liquid phase. In the case of solutions of these organic compounds also, we should expect such a change in susceptibility.

In the present investigation, the susceptibilities of two important organic compounds, benzophenone and paranitrotoluene are studied in

the dissolved state, the solvent chosen being methyl alcohol. There are special reasons for choosing them for this investigation. If the substances studied by Oxley be examined, it will be found that most of them are liquids at room temperatures. But benzophenone and paranitrotoluene exist as solids at room temperatures and their melting points are not far removed from the ordinary temperatures. The melting point of benzophenone is 48°C . and that of paranitrotoluene 54°C . Hence these substances can be studied in the solid, dissolved and liquid (molten) states conveniently. Again they show opposite behaviour on melting, benzophenone shows an increase in susceptibility value on fusion while paranitrotoluene shows a decrease.

Oxley records an increase of 6% on fusion in the case of benzophenone. Krishnan, Guha and Banerjee,⁵ on the other hand, find a change of only $2\frac{1}{2}\%$. The latter authors interpret the large changes observed by Oxley as due to the effects of preferential orientation of microcrystals of the solid in the magnetic field. It appears doubtful whether this will completely explain Oxley's results. To investigate the problem at some length, experiment was undertaken to study the change of susceptibility on melting in the case of these two compounds.

Cabrera and Fahlenbrach⁶ have also recently studied the changes during melting in the case of some organic compounds including paranitrotoluene. They record a decrease of about 4.3% for this compound on melting.

Incidentally, in the case of benzophenone a study of the supercooled state was made possible by the fact that benzophenone remains in the liquid condition even when it is cooled to room temperature. This is of special interest since the susceptibility value in the supercooled state was found to be slightly higher than that for the solid state.

2 Experiment

The investigations were carried out with a Curie balance, the retorsion method being employed to take the deflections. Water was chosen as the standard, and its susceptibility was assumed to be 0.72.* The measurements were thoroughly standardised and the error does not exceed $\frac{1}{2}\%$.

Benzophenone and paranitrotoluene of superior quality crystallised from pure methyl alcohol, were used in the experiments. Small thin bulbs which could be stoppered tightly were used for filling up the solutions and finding the deflections. After taking the deflections, the bulbs were kept open and the solution allowed to evaporate and deposit crystals. The

* All susceptibility values in this paper are to be multiplied by 10^{-6} .

bulbs were then weighed and thus the concentrations of the solutions were determined.

3. Results.

The susceptibility values of benzophenone, paranitrotoluene and methyl alcohol are given below along with those of other investigators.

TABLE I.

Substance	Author χ	Krishnan, Guha and Banerjee χ	Cabrera and Fahlenbrach χ	Kido ⁷ χ	Int. ⁸ Crit. Tables χ
Benzophenone ..	0.600	0.594	0.594
Paranitrotoluene	0.518	..	0.538
Methyl alcohol ..	0.685	..	0.674*	0.696	..

* *Zeit f. Phys*, 1933, **85**, 568.

The values obtained in this investigation are found to agree very satisfactorily with those of other investigators.

I. *Change in Solution.* (a) *Benzophenone*—The results for the solution of benzophenone in methyl alcohol are given in Table II.

TABLE II.

Expt. No.	Weight of solution gr.	Wt. of benzo- phenone dissolved gr.	Concen- tration per cent.	Solution χ	Cal. χ	$\chi_{\text{Sol}} - \chi_{\text{Cal.}}$	Differ- ence for 100 %
1	0.0489	0.0114	23.3	0.670	0.665	+0.005	+0.022
2	0.0819	0.0215	26.2	0.668	0.663	+0.005	+0.020
3	0.0664	0.0368	55.4	0.644	0.638	+0.006	+0.011
4	0.0924	0.0545	59.0	0.638	0.633	+0.005	+0.009
5	0.0733	0.0501	68.3	0.639	0.627	+0.012	+0.018
6	0.0818	0.0651	79.6	0.630	0.618	+0.012	+0.015

The sixth column gives the value of susceptibility calculated on the basis of the additive law and the seventh gives the difference. The last column gives difference in susceptibility value of benzophenone in solution and in the solid state.

On looking at the table, it is seen that there is a definite departure from the additive law. A large number of observations were taken of which six typical values are given above

The average value of the last column (the difference between the susceptibility values of benzophenone in solution and in solid) works to 0.016. Hence the change in susceptibility in solution is $+0.016$. Its susceptibility in solution is therefore $0.600 + 0.016 = 0.616 \pm 0.006$.

(b) *Paranitrotoluene*.—The results for paranitrotoluene-methyl alcohol solutions are given in Table III

TABLE III.

Concen- tration Number	Wt. of solution gr.	Wt. of substance dissolved gr.	Concen- tration per cent.	Soln. χ	Cal. χ	$\chi_{\text{Sol}} - \chi_{\text{Cal}}$
1	0.0808	0.0179	20.2	0.641	0.648	— 0.007
2	0.0611	0.0130	21.3	0.640	0.650	— 0.010
3	0.0702	0.0172	24.2	0.630	0.645	— 0.015
4	0.0686	0.0197	28.7	0.628	0.637	— 0.009
5	0.0605	0.0174	28.8	0.632	0.637	— 0.005
6	0.0631	0.0200	31.7	0.624	0.632	— 0.008

In this case, it is observed that the susceptibility value of paranitrotoluene in the dissolved state is less than that in the solid state. The average value of the last column ($\chi_{\text{Soln.}} - \chi_{\text{Cal}}$) is found to be 0.009 and since the concentrations are only within a short range of 20 to 32% we may take the mean concentration to be nearly 26%. Hence the total change in value for paranitrotoluene in solution is $\frac{.009}{26} \times 100$; that is, $0.035 \pm .005$ and the susceptibility of the solid in solution is $0.483 \pm .005$.

II. *Change on Melting*. (a) *Benzophenone*.—Benzophenone was taken in a sealed bulb and suspended in the magnetic field inside a heater.

An initial reading was taken at room temperature and a small current was sent through the heater. The deflections were noted as the temperature gradually increased. Up to 48°C ., the melting point of benzophenone, no change was observed. At 48°C . there was an increase in deflection (equivalent to 4.8%). Afterwards it remained constant up to 120°C . the maximum temperature reached in this experiment.

It was very interesting to study the changes during the process of cooling. With the gradual cooling of the substance below 48°C ., a gradual decrease as distinct from a sudden decrease in value in passing through the melting point observed before, was noted. At room temperature (30°C .) the value of the supercooled liquid was definitely higher than the value in the solid state by 1.2%. The bulb was taken out and shaken to solidify the substance and it was found to have regained the original deflection for the solid state. These changes are shown by means of a graph. (See Fig. 1.)

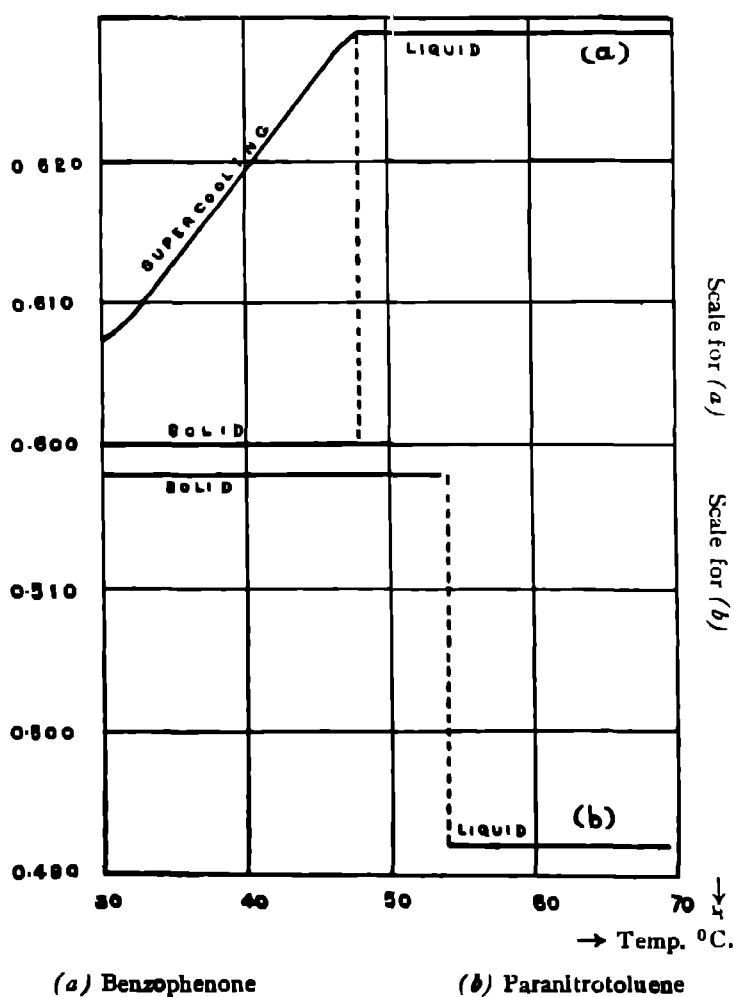


FIG. 1.

(b) *Paranitrotoluene*.—Here a decrease of 5.1% was observed at the melting point (54° C.). The susceptibility remained constant up to and above the melting point. No such under-cooling effect as obtained in the case of benzophenone was observed. The substance began to crystallise as soon as the temperature fell below the melting point. The changes are shown by a graph. The results are given in Table IV.

TABLE IV.

Substance	Solid χ	Liquid χ	Change %
Benzophenone	0.600	0.629	+ 4.8
Paranitrotoluene	0.518	0.492	— 5.1

Cabrera and Fahlenbrach noted a change of 4.3% in the case of paranitrotoluene. They have studied undercooling in the case of ortho- and para-cresols. But they do not obtain such gradual decrease as observed here in the case of benzophenone. The susceptibility remains constant and equal to the value for the fused state in both cases.

4 Discussion

Benzophenone and paranitrotoluene, the two substances investigated here, show the same order of susceptibility changes in solution as on melting. There is every reason to believe that other substances whose susceptibility alters on melting would similarly show a change in solution provided the proper solvents are chosen.

In a recent paper, Varadachari⁹ has advanced the view that in a solid, there are polymers present which partially or completely decompose on melting. It is well known that a polymer, as distinguished from an associated complex, has got a definite structure and hence when a polymer decomposes there is a disruption of its structure as a consequence of which, there will be a change in susceptibility. Hence those solids which show a change in susceptibility on melting may be assumed to contain polymers which decompose on fusion. If a substance shows a temperature variation in susceptibility in the liquid state it is likely that the depolymerisation is only partial on melting and that the depolymerisation continues even above the melting point. As the temperature of the liquid is raised, the depolymerisation becomes complete at a specific temperature when no more polymers are present. The susceptibility will remain constant above that temperature. This has been observed by Cabrera and Fahlenbrach¹⁰ in the

case of water which is known to contain various polymers in different proportions depending on the temperature. The susceptibility slightly increases with temperature and attains a constant value above 120°C . showing that above that temperature, water exists as simple molecules.

A similar theory can be extended to the state of solution, since we also observed a change in the susceptibility of the dissolved substance in such cases. However, the case of solutions is not so simple as that of melting. Solutions are complicated by the fact that the solute molecules (or the ions into which they may get dissociated) are surrounded by the molecules of the solvent which may introduce new linkages. In such a case, the change in susceptibility that we observe will depend on the medium in which the substance is dissolved. But in solutions which we have investigated, such conditions may not exist and the theory of decomposition of polymers will sufficiently explain the results

It may be mentioned here that a study of the Raman effect of these substances in various physical states will give important and interesting results. Much information does not seem to be available in this direction. Raman effect data, coupled with the results of magnetic investigations, are bound to throw more light on the nature of solutions.

It is observed here that a change of about 5% in susceptibility value occurs in the case of benzophenone during melting. This agrees with that observed by Oxley. Krishnan, Guha and Banerjee, on the other hand, find a change of only 2.5%. These authors deduce the mean susceptibility of the substance from the three principal susceptibilities of the single crystal and compare this with the susceptibility value of the molten substance obtained by employing a different method

These authors explain this discrepancy by suggesting that the orientations of the micro-crystals of the substance cannot be at random on account of the strong anisotropy of the crystal when the solids are obtained by cooling the liquid in a magnetic field. Goetz¹¹ who has made a special study of metallic crystals, has studied the effect of magnetic field on the growth of single crystals of bismuth. He found that crystals grown without a pre-determined orientation indicated a preference for an orientation in which the direction of the smallest diamagnetic susceptibility was parallel to the lines of force. He used a field of 20,000 gauss and he observed that this effect was much smaller than the orienting forces of a seed-crystal. It only proves the existence of micro-crystals even slightly above the melting point. The field that we ordinarily employ is even considerably less than 20,000 gauss (the author has worked with a magnetic field of 5,000 gauss) and hence the orientation effect due to the field in these cases must be very

small and probably even negligible. It is difficult to believe therefore whether the large change observed by Oxley and others can be explained by this effect. The change therefore appears to be genuine.

Cabrera and Fahlenbrach⁶ have tried to find a relation between the change of susceptibility at the melting point and the dipole moment of the substance concerned. They plot a graph between $(\chi_{\text{liquid}} - \chi_{\text{solid}})$ and the dipole moment and draw a smooth curve passing evenly through the plotted points. The evidence however is not convincing. The points plot themselves at random. Besides, they have not studied substances of very high dipole moments which should show large changes on melting according to their theory. Further the force due to the dipole moment is only a body force and does not affect the electron system as has been proved in the case of liquid mixtures.¹² It is therefore difficult to suggest a definite relation between dipole moment and change in susceptibility on fusion. The explanation on the basis of break-up of polymers seems to be nearest the truth.

Summary

Benzophenone and paranitrotoluene have been studied in the solid and fused states. Their solutions in methyl alcohol have also been investigated and the changes of susceptibility on dissolving solution are found to be in the same direction as those on melting. The supercooled state in the case of benzophenone has also been examined. The experiments lend support to the theory that the changes on melting and solution could be attributed to the break-up of polymers present in the solid state.

I take this opportunity of thanking Dr. S. Ramachandra Rao for his interest and guidance. My thanks are also due to the authorities of the Annamalai University for the award of a studentship

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MAGNETIC STUDIES OF SULPHUR AND SOME SULPHUR COMPOUNDS.

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1. Introduction

It is well known that sulphur exists in various complexes. X-ray analysis¹ in rhombic crystals shows that the molecule of sulphur in the crystal exists as S_{16} . The nature of sulphur complexes has also been investigated in various solutions by studying their vapour pressures and molecular weights.² One of the objects of the present investigation is to determine the state of sulphur in solutions purely by magnetic method.

Krishnamurti³ studied the Raman spectrum of rhombic sulphur in the form of small crystals. On dissolving sulphur in carbon disulphide he found that one of the lines attributed to the S_{16} molecule disappeared. He also records three strong lines as present both in solid and in solution and attributes them to S_8 molecules. We have chosen carbon disulphide and sulphur monochloride as the solvents since sulphur has a high solubility in these liquids (about 55% and 65% respectively at room temperature). The evidence from vapour pressure measurements on the state of sulphur in solutions of sulphur monochloride is not conclusive. Some measurements point to the existence of S_2 in the solution while others indicate the presence of S_8 molecules.⁴ A study of this solution was therefore undertaken with a view to throw some light on this question.

Compounds of sulphur also present an interesting study, because of the different valencies exhibited by the element in chemical combination. Pascal⁵ was the first to study the magnetic susceptibilities of several sulphur compounds. More recently a few compounds of sulphur were studied by Farquharson⁶ with the Curie-Cheneveau balance. Kido⁷ also investigated a number of sulphur compounds and derived susceptibility values for several incomplete ions of sulphur. His study also included a number of homopolar compounds from which he established the applicability of the additive law to such compounds.

Varadachari⁸ studied the diamagnetic susceptibilities of crystalline sulphates of lithium, sodium, potassium and magnesium. His results show that the nature of the bond between the water molecules and the sulphate ion is a loose one. Sodium and potassium sulphides were also investigated by him. A graph drawn between the susceptibility of different incomplete sulphur ions and the valency of sulphur gave a straight line thus confirming Kido's result.

We have studied the mono- and di-chlorides of sulphur, thionyl and sulphuryl chlorides and sulphur iodide and the results we have obtained are of special interest from the point of view of their molecular structure.

2. *Experiment.*

Susceptibility measurements were made with a Curie balance, the retorsion method being employed to bring the specimens in the identical position with the field on. Water was chosen as the standard substance, its susceptibility being taken as 0.72.* The substances were contained in thin glass bulbs provided with air-tight stoppers. The bulbs were weighed before and after the deflections were taken to detect losses by evaporation in the case of liquids.

Sulphur crystals were purified by crystallising from solutions in pure distilled carbon disulphide. The substances used were of the purest quality obtained from Kahlbaum or Merck. An average deflection of about 20 cm. was obtained in most cases. The deflection of the standard bulbs was taken before and after each experiment to correct for any errors that may arise from fluctuations in the constants of the apparatus.

Solutions of sulphur in carbon disulphide were studied for various concentrations. The bulbs were filled with the solutions, stoppered tightly, weighed and suspended from the Curie balance. After noting the deflection the bulbs were left open for a time to allow the liquid to evaporate away, and the deposited sulphur weighed. The concentrations of the solutions were thus determined.

In the case of sulphur solutions in its monochloride, the determination of the concentrations is not so easy, since sulphur monochloride hydrolyses on exposure to air and leaves sulphur behind. We have taken weighed quantities of the solute and the solvent and believe that the concentrations of the solutions investigated should have been between 50 and 60%.

3. *Results.*

(a) *Sulphur in carbon disulphide.*—The diamagnetic susceptibility of carbon disulphide was found to be 0.556. This agrees very closely with the

* In this paper all the susceptibility values must be multiplied by 10^{-6} .

value of 0.54 given in the *International Critical Tables*; as well as 0.565 of one of us,⁸ and 0.550 of Rao and Sivaramakrishnan.⁹ For sulphur we obtained 0.457. We may mention that this is slightly less than 0.485 obtained by Owen,¹⁰ 0.487 by Bhatnagar and Mathur¹¹ and 0.481 by one of us.⁸

The results obtained with solutions of sulphur in carbon disulphide having concentrations varying from about 12 to 56% are given below. The calculated values of the diamagnetic susceptibility of the solutions based on the assumption of the additive law are given in the sixth column. In the last column the difference between the observed and calculated values are shown.

Concentration No.	Weight of solution	Weight of sulphur dissolved	Concentration per cent.	Solution χ	Calculated χ	$\chi_{\text{Solution}} - \chi_{\text{Calculated}}$
	Gm.	Gm.				
1	0.0974	0.0117	12.0	0.546	0.544	+0.002
2	0.0666	0.0134	20.1	0.540	0.536	+0.004
3	0.0661	0.0146	22.1	0.532	0.534	-0.002
4	0.0662	0.0160	24.2	0.538	0.532	+0.006
5	0.0978	0.0292	29.9	0.529	0.526	+0.003
6	0.1032	0.0334	32.4	0.529	0.524	+0.005
7	0.0984	0.0342	34.8	0.526	0.521	+0.005
8	0.0709	0.0250	35.3	0.524	0.521	+0.003
9	0.0895	0.0359	40.1	0.520	0.516	+0.004
10	0.0717	0.0297	41.4	0.520	0.515	+0.005
11	0.0900	0.0390	43.4	0.521	0.513	+0.008
12	0.1041	0.0455	43.7	0.513	0.513	+0.000
13	0.1223	0.0535	43.7	0.520	0.513	+0.007
14	0.0763	0.0414	54.3	0.509	0.502	+0.007
15	0.1526	0.0858	56.2	0.506	0.500	+0.006

It will be noted that the difference in the last column is in most cases within the limits of error. But sometimes the deviation works to as much as 1.5% from which it appears to follow that small alterations in the diamagnetic susceptibility accompany the breaking down of the S_{16} complex into lower complexes in solution. A more careful scrutiny of the results suggests that such a deviation may be genuine; for, if there be a change of about 1% in solution, the deviations in the last column would tend to lie between $\frac{1}{2}$ and $1\frac{1}{2}$ per cent., on the assumption that the error in our results is $\frac{1}{2}$ %. In most cases, this is just what is found. We may therefore conclude that the breaking down of the S_{16} complex is accompanied by an increase in the diamagnetic susceptibility. Such an increase has a theoretical background in the fact that the Van Vleck¹² paramagnetic term would show a decrease in value when the complex breaks down.

(b) *Sulphur in sulphur monochloride*.—Sulphur monochloride appeared yellowish red and fumed in air. The average diamagnetic susceptibility of the liquid was found to be 0.461. We have not been able to find any previous measurements for this liquid

As mentioned earlier in this paper, concentrated solutions of sulphur in its monochloride were prepared and investigated. The results obtained with half a dozen solutions are given below.

Experiment number	Weight of solution Gr.	Solution χ
1	0.1099	0.462
2	0.1090	0.458
3	0.1075	0.458
4	0.1020	0.461
5	0.0672	0.458
6	0.1322	0.462

The value of the susceptibility of the solution remains the same as that of sulphur (0.457) and sulphur monochloride (0.461). Orndorff and Terrasse¹³ suggest from their investigations based on boiling point determinations that sulphur exists as S_8 in sulphur monochloride. It is well known that S_8 like O_8 is paramagnetic. Our results do not indicate any deviation in the susceptibility and hence it may be concluded that no S_8 molecules are formed when sulphur is dissolved in its monochloride.

The solutions contained in small bulbs were heated to temperatures up to about 120° C. and the susceptibilities at different temperatures determined. No change in the susceptibility was observed indicating that the elevation of temperature does not favour the production of S_2 complex.

(c) *Compounds of sulphur*.—The following compounds have been studied, sulphur monochloride, sulphur dichloride, thionyl chloride, sulphuryl chloride and sulphur iodide. The results are shown in the accompanying table. In column 2 are shown the structural formulæ supported by magnetic evidence. The calculated values of the molecular susceptibility given in the last column have been calculated from the ionic values given by Kido.

Kido's Values.

Ion	Molecular susceptibility
S^{-2}	27.4
S^0	(14.6)*
S^{+2}	5.2
S^{+4}	−4.6
S^{+6}	−15.0
Cl^{-1}	22.1
O^{-2}	13.7
I^0	44.4†

* The value is ours.

† Value taken from *Int. Crt. Tables*.

Compound	Structure	Diamagnetic mass susceptibility	Diamagnetic Molecular susceptibility	
			Observed	Calculated
S_2Cl_2	$S = S \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	0.461	62.2	67.0
SCl_2	$S \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	0.467	48.1	49.4
$SOCl_2$	$O = S \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	0.372	44.3	53.3
SO_2Cl_2	$O \begin{matrix} \diagup \\ \diagdown \end{matrix} S \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$	0.365	49.3	56.6
SI	$S + I$	0.329	52.7	54.0

It will be seen that in the second case, the calculated and observed values nearly agree. However, the difference is somewhat greater in the case of the monochloride. This may be attributed to the stronger binding between the two sulphur atoms.

Such a striking difference exists also in the case of thionyl chloride. This departure may again be due to a strong binding between the sulphur and oxygen atoms, which introduces ionic deformation and consequently a high paramagnetic term in the total molecular susceptibility. The diamagnetic susceptibility of the compound is thus reduced and the magnitude of the difference between the observed and calculated values may be taken as a measure of the strength of binding between the atoms in the molecule.

The case of sulphuryl chloride is of special interest since sulphur in this molecule has been considered as tetravalent by some chemists and hexavalent by others. The magnetic data support the latter view. For, if sulphur was tetravalent its molecular susceptibility would work to 67.0 as against 56.6 shown in our tables.

Considerable evidence on chemical grounds has been advanced in support of the view that all the so-called sulphur iodides are only mixtures of sulphur and iodine.¹⁴ Our results also support this view. If sulphur iodide is a compound with the molecular structure $S=S\begin{matrix} I \\ \diagdown \\ I \end{matrix}$ then the molecular susceptibility of SI would work to 64.6 as against the observed value of 52.7. On the other hand, assuming SI to be a mixture, the molecular susceptibility is calculated to be 54.0 which agrees closely with the observed value. Some investigators have suggested that the substance has the characters of metal alloys and that the mono-iodide is in a feeble state of combination. These conclusions are entirely supported by our results.

4 Summary.

Solutions of sulphur in carbon disulphide and sulphur monochloride have been studied by the Curie method. Small deviations of the order of 1 per cent have been observed for solutions in carbon disulphide. This has been attributed to the breaking down of S_8 molecule. No evidence has been obtained to indicate the presence of S_2 in sulphur monochloride solutions. A few halides of sulphur have also been investigated. The results throw useful light on the valency of sulphur in the different compounds.

We take this opportunity of thanking the authorities of the Annamalai University for the award of studentships which enabled us to undertake this investigation. Our thanks are also due to Dr. S. Ramachandra Rao for his interest in this work.

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VORTEX MOTION IN RECTANGULAR CYLINDERS.

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THE general problem of the motion of a liquid due to a rectilinear vortex in a cylinder whose cross-section is bounded by four arcs of mutually orthogonal curves can be readily solved with the help of conformal transformation. By considering the infinite series of images in the four bounding planes Greenhill¹ has solved two particular cases. From his analysis it appears that this method of images is bound to be rather long and inconvenient in the general case. Moreover it is not always free from preliminary limitations which may not be found essential when the solution of the problem has been obtained. For example, in the case of a rectangle bounded by two concentric arcs and two radii inclined at an angle $\frac{1}{n}\pi$ Greenhill has to make the supposition in the beginning that $\frac{1}{n}\pi$ is a sub-multiple of two right angles. As he remarks at the end of his paper his solution holds good whatever $\frac{1}{n}\pi$ may be.²

We take the plane of a cross-section as the plane of a complex variable z . Let a system of orthogonal curves in the z -plane be given by

$$\omega = \alpha + i\beta = f(z);$$

so that the sides of the z -rectangle can be taken as $\alpha = 0$, $\alpha = 2K$, $\beta = 0$, and $\beta = 2K'$, K and K' being two constants. The ω -rectangle can be mapped on a ζ -half plane by means of the relation

$$\omega = A \int [(\zeta - \xi_1)(\zeta - \xi_2)(\zeta - \xi_3)(\zeta - \xi_4)]^{-\frac{1}{2}} d\zeta + B, \quad \dots \quad (1)$$

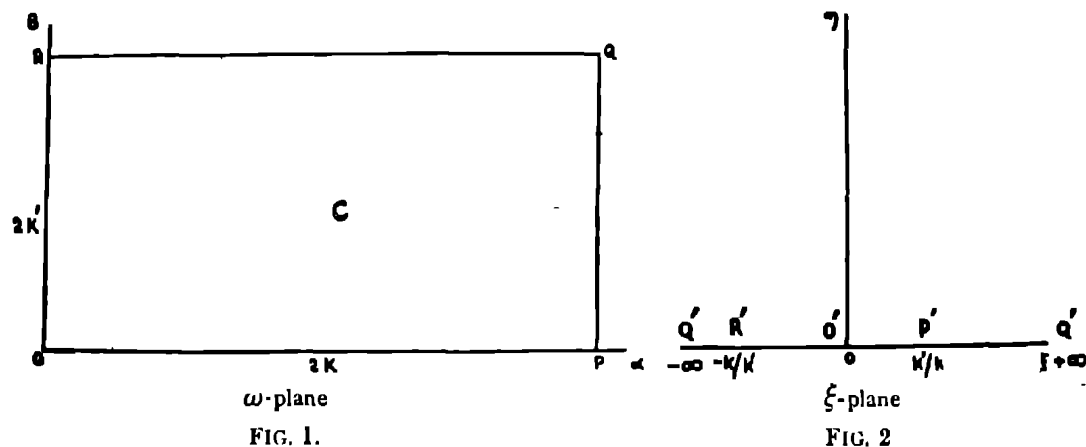
ξ_1 , ξ_2 , ξ_3 , and ξ_4 being the points on the real axis in the ζ -plane that correspond to the angular points P, Q, R, and O in the ω -plane.

Putting $\xi_1 = k'/k$, $\xi_2 = \infty$, $\xi_3 = -k/k'$, and $\xi_4 = 0$, we get

$$\omega = A \int [\zeta(\zeta + k/k')(\zeta - k'/k)]^{-\frac{1}{2}} d\zeta + B.$$

¹ Greenhill, *Quart. J. of Math.*, 1877, 15, 23-29.

² This limitation in the method of images has been pointed out by Ramsey in his *Hydro-mechanics*, Part 2, Art. 189, (1913) edition.



Adjusting the constants A and B we can write³

$$\zeta = -k/k' \operatorname{Cn}^2 \left(\frac{1}{2} \omega - K - iK' \right) = k'/k \operatorname{nc}^2 \left(\frac{1}{2} \omega \right) \quad \dots \quad (2.1)$$

$$= \frac{k \operatorname{dn} \omega - \operatorname{Cn} \omega}{k' (1 - \operatorname{dn} \omega)}, \quad \dots \quad (2.2)$$

k being the modulus, and $4K$, $4iK'$ the periods of the elliptic function. Referred to C, the centre of the ω -figure, as the origin this transformation becomes

$$\zeta = \frac{i(1 + k \operatorname{Sn} \omega)}{\operatorname{Cn} \omega - i k' \operatorname{Sn} \omega} \quad \dots \quad (2.3)$$

Hence the relation

$$\zeta = \frac{i[1 + k \operatorname{Sn} \{f(z)\}]}{\operatorname{Cn} \{f(z)\} - i k' \operatorname{Sn} \{f(z)\}} \quad \dots \quad (3)$$

transforms the z -rectangle into the upper half of the ζ -plane.

Let there be a vortex of strength m at a point z_0 within the z -rectangle, and let ω_0 and ζ_0 be the corresponding points of the ω -plane and ζ -plane. If ϕ is the velocity potential and ψ the stream function of the motion, we know that

$$\phi + i\psi = \frac{mi}{2\pi} \log \frac{\zeta - \zeta_0}{\zeta - \zeta_0'}, \quad \dots \quad (4)$$

which, after using (2.1), becomes

$$\phi + i\psi = \frac{mi}{2\pi} \log \frac{\operatorname{Cn}^2 \frac{1}{2} \{f(z_0')\} [\operatorname{Cn}^2 \frac{1}{2} \{f(z)\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0)\}]}{\operatorname{Cn}^2 \frac{1}{2} \{f(z_0)\} [\operatorname{Cn}^2 \frac{1}{2} \{f(z)\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0')\}]}, \quad (5)$$

where $\zeta_0' = \xi_0 - i\eta_0$ and $z_0' = x_0 - iy_0$. The stream function is, therefore, given by

$$\psi = \frac{m}{4\pi} \log \frac{[\operatorname{Cn}^2 \frac{1}{2} \{f(z)\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0)\}] [\operatorname{Cn}^2 \frac{1}{2} \{f(z')\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0')\}]}{[\operatorname{Cn}^2 \frac{1}{2} \{f(z)\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0')\}] [\operatorname{Cn}^2 \frac{1}{2} \{f(z')\} - \operatorname{Cn}^2 \frac{1}{2} \{f(z_0)\}]} \quad \dots \quad (6)$$

³ We have followed Dr. Glaisher in writing $\operatorname{ncu} = 1/\operatorname{cnu}$, with a similar notation for the other elliptic functions.

To determine the curve described by the vortex we apply the well-known result due to Routh,⁴ viz.

$$\chi(x, y) = \chi(\xi, \eta) + \frac{m}{4\pi} \log \left| \frac{d\zeta}{dz} \right|, \quad \dots \quad (7)$$

$\chi(x, y)$ being the stream function for the motion of the vortex in the z -plane and $\chi(\xi, \eta)$ of the corresponding vortex in the ζ -plane. From (4) we easily get

$$\chi(\xi, \eta) = -\frac{m}{4\pi} \log \eta. \quad \dots \quad (8)$$

η and $|d\zeta/dz|$ can be determined either from (2.2) or from (3) according as O or C in Fig. 1 is taken as the origin. Taking (2.2) we have

$$\begin{aligned} 2i\eta &= \frac{k}{k'} \left[\frac{dn \omega - Cn \omega}{1 - dn \omega} - \frac{dn \omega' - Cn \omega'}{1 - dn \omega'} \right] \\ &= \frac{k}{k'} \left[\frac{(dn \omega - dn \omega') - (Cn \omega - Cn \omega') + (Cn \omega dn \omega' - Cn \omega' dn \omega)}{(1 - dn \omega)(1 - dn \omega')} \right], \end{aligned}$$

which, after using Jacob's addition formulæ⁵ for the various terms in square brackets, becomes

$$\begin{aligned} 2i\eta &= -\frac{k}{k'} \frac{Sn \alpha Sn i\beta (k'^2 + k^2 Cn \alpha Cn i\beta - dn \alpha dn i\beta)}{(dn \alpha - dn i\beta)^2} \\ &= -\frac{k}{k'} \frac{Sn \alpha Sn i\beta}{Cn \alpha + Cn i\beta} \cdot \frac{dn \alpha Cn i\beta - dn i\beta Cn \alpha}{dn \alpha - dn i\beta} \quad \dots \quad (9) \end{aligned}$$

Again we have

$$\left| \frac{d\zeta}{dz} \right|^2 = \left| \frac{d\zeta}{d\omega} \cdot \frac{d\omega}{dz} \right|^2 = \left| \frac{d\zeta}{d\omega} \right|^2 f'(z) f'(z'),$$

where $f'(z) = d\{f(z)\}/dz$. Using (2.1) we get

$$\left| \frac{d\zeta}{d\omega} \right|^2 = \frac{k'^2}{k^2} \cdot \frac{Sn \frac{1}{2} \omega Sn \frac{1}{2} \omega' dn \frac{1}{2} \omega dn \frac{1}{2} \omega'}{Cn^3 \frac{1}{2} \omega Cn^3 \frac{1}{2} \omega'}.$$

Since⁶

$$Sn \frac{1}{2} \omega Sn \frac{1}{2} \omega' = \frac{1}{k^2} \cdot \frac{dn i\beta - dn \alpha}{Cn i\beta - Cn \alpha},$$

$$Cn \frac{1}{2} \omega Cn \frac{1}{2} \omega' = \frac{k'^2}{k^2} \cdot \frac{dn i\beta - dn \alpha}{Cn i\beta dn \alpha - Cn \alpha dn i\beta},$$

$$dn \frac{1}{2} \omega dn \frac{1}{2} \omega' = k'^2 \frac{cn i\beta - cn \alpha}{cn i\beta dn \alpha - cn \alpha dn i\beta},$$

⁴ Routh, *Proc. London Math. Soc.*, 1881, 12, 82-84; also Ramsey *Hydromechanics*, Part 2, pp. 224-5 (1913 edition).

⁵ See Cayley, *Elliptic Functions*, 1876, 65-66.

⁶ For these formula reference may be made to Greenhill, *Applications of Elliptic Functions*, (1892), 255.

we have

$$\left| \frac{d\zeta}{d\omega} \right|^2 = \frac{k^2}{k'^2} \cdot \frac{\text{Cn } i \beta - \text{Cn } a}{\text{Cn } i \beta + \text{Cn } a} \cdot \frac{(\text{Cn } i \beta \, dn \, a - \text{Cn } a \, dn \, i \beta)^2}{(dn \, a - dn \, i \beta)^2}, \quad \dots \quad (10)$$

and hence (7) and (8) give

$$\begin{aligned} \chi(x, y) &= \frac{m}{8\pi} \log \frac{4(\text{Cn}^2 a - \text{Cn}^2 i \beta)}{\text{Sn}^2 a \, \text{Sn}^2 \beta} f'(z) f'(z') \\ &= \frac{m}{8\pi} \log 4 (n\text{S}^2 a - n\text{S}^2 i \beta) f'(z) f'(z') \\ &= \frac{m}{8\pi} \log 4 [n\text{S}^2(a, k) + n\text{S}^2(\beta, k') - 1] f'(z) f'(z') \quad \dots \quad (11) \end{aligned}$$

If we put

$$\omega = a + i \beta = f(z) = f_1(x, y) + i f_2(x, y),$$

we get

$$\begin{aligned} \chi(x, y) &= \frac{m}{8\pi} \log 4 [n\text{S}^2 \{f_1(x, y), k\} + n\text{S}^2 \{f_2(x, y), k'\} - 1] \\ &\quad \times f'(z) f'(z'); \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (12) \end{aligned}$$

so that the curve described by the vortex is given by

$$[n\text{S}^2 \{f_1(x, y), k\} + n\text{S}^2 \{f_2(x, y), k'\} - 1] f'(z) f'(z') = \text{a constant.} \quad (13)$$

When the rectangle in the z -plane is rectilinear we have $\omega = z$, and the stream lines are given from (6) as

$$\frac{(cn^2 \frac{1}{2} z - cn^2 \frac{1}{2} z_0) (cn^2 \frac{1}{2} z' - cn^2 \frac{1}{2} z'_0)}{(cn^2 \frac{1}{2} z - cn^2 \frac{1}{2} z'_0) (cn^2 \frac{1}{2} z' - cn^2 \frac{1}{2} z_0)} = \text{constant.}$$

The curve described by the vortex is

$$ns^2(x, k) + ns^2(y, k') = \text{a constant}^7 \quad \dots \quad \dots \quad \dots \quad (14)$$

Referred to the centre of the rectangle as origin it becomes

$$k'^2 nc^2(x, k) + k^2 nc^2(y, k') = \text{a constant} \quad \dots \quad \dots \quad \dots \quad (15)$$

For a square cross-section we have

$$K = K' = 1.854; \quad k = k' = 1/\sqrt{2},$$

and (15) reduces to

$$nc^2(x, k) + nc^2(y, k) = c \text{ (say).}$$

In Fig. 3 I have traced some of these curves in the first quadrant by taking $c = 3, 4, 7, 31$. Obviously these curves are symmetrical both about the co-ordinate axes and the lines $x \pm y = 0$.

The vortex is stationary when at the centre of the rectangle. Using (3) and (4) and noticing that $\zeta = i$ corresponds to $z = 0$ we get

⁷ This result is the same as obtained by Greenhill, *loc. cit.*, 25.

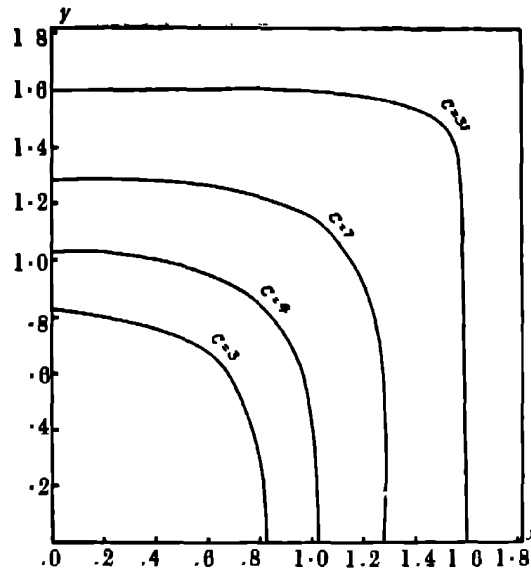


FIG. 3.

$$\begin{aligned}
 \phi + i\psi &= \frac{mi}{2\pi} \log \frac{\zeta - i}{\zeta + i} \\
 &= \frac{mi}{2\pi} \log \frac{1 - \operatorname{Cn} z + (k + i k') \operatorname{Sn} z}{1 + \operatorname{Cn} z + (k - i k') \operatorname{Sn} z} \\
 &= \frac{mi}{2\pi} \log \frac{(k + i k') \operatorname{Sn} z}{1 + \operatorname{Cn} z} = \frac{mi}{4\pi} \log \frac{1 - \operatorname{Cn} z}{1 + \operatorname{Cn} z}, \quad \dots \quad (16)
 \end{aligned}$$

neglecting a constant.

The stream function⁸ of the motion is given by

$$\begin{aligned}
 \psi &= \frac{m}{8\pi} \log \frac{(1 - \operatorname{Cn} z)(1 - \operatorname{Cn} z')}{(1 + \operatorname{Cn} z)(1 + \operatorname{Cn} z')} \\
 &= \frac{m}{4\pi} \log \frac{\operatorname{Cn} x - \operatorname{Cn} i y}{\operatorname{Cn} x + \operatorname{Cn} i y} = \frac{m}{2\pi} \tanh^{-1} \frac{\operatorname{Cn} x}{\operatorname{Cn} i y} \\
 &= \frac{m}{2\pi} \tanh^{-1} \{\operatorname{Cn}(x, k) \operatorname{Cn}(y, k')\} \quad \dots \quad \dots \quad (17.1)
 \end{aligned}$$

In like manner

$$\phi = -\frac{m}{2\pi} \tan^{-1} \frac{\operatorname{Sn}(x, k) \operatorname{dn}(y, k')}{\operatorname{Sn}(y, k') \operatorname{dn}(x, k)} \quad \dots \quad \dots \quad (17.2)$$

The equation of the stream lines is, therefore, given by

$$\operatorname{Cn}(x, k) \operatorname{Cn}(y, k') = \text{a constant} = c \text{ (say)} \quad \dots \quad \dots \quad (18)$$

By taking $c = .1, .25, .5, .75$, I have traced the corresponding stream lines in Fig. 4 for the first quadrant of a square cross-section.

⁸ Greenhill, *loc. cit.*, 26.

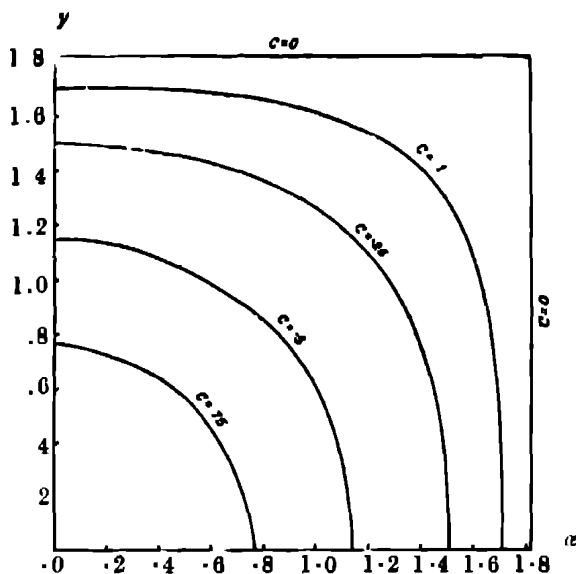


FIG. 4

When the cross-section is bounded by two concentric arcs of radii a and b , and two radii inclined at an angle ϵ we have the relation

$$\omega = \alpha + i\beta = \frac{2K'}{\epsilon} \log \frac{z}{a} = \frac{2K'}{\epsilon} \left(\log \frac{r}{a} + i\theta \right) \quad \dots \quad (19)$$

where it is assumed that $\alpha = 0$, $\alpha = 2K$, $\beta = 0$, $\beta = 2K'$ correspond with $r = a$, $r = b$, $\theta = 0$, $\theta = \epsilon$ respectively. (6) and (13) give the stream function of the motion as

$$\psi = \frac{m}{4\pi} \log \frac{[Cn^2 \{(K'/\epsilon) \log (z/a)\} - Cn^2 \{K'/\epsilon \log (z_0/a)\}]}{[Cn^2 \{(K'/\epsilon) \log (z/a)\} - Cn^2 \{K'/\epsilon \log (z_0'/a)\}]} \times \frac{[Cn^2 \{(K'/\epsilon) \log (z'/a)\} - Cn^2 \{K'/\epsilon \log (z_0'/a)\}]}{[Cn^2 \{(K'/\epsilon) \log (z'/a)\} - Cn^2 \{K'/\epsilon \log (z_0/a)\}]} \quad (20)$$

and the curve described by the vortex as

$$\frac{1}{r^2} \left[nS^2 \left(\frac{2K'}{\epsilon} \log \frac{r}{a}, k \right) + nS^2 \left(\frac{2K'\theta}{\epsilon}, k' \right) - 1 \right] = \text{a constant} \quad \dots \quad (21)$$

a result quite laboriously obtained by Greenhill.⁹

I do not think Greenhill is right when he says that the vortex is stationary when $r = \sqrt{ab}$, $\theta = \frac{1}{2}\epsilon$. This can be easily seen from (11) if we form the values of $\partial\chi/\partial x$ and $\partial\chi/\partial y$. What actually happens is that the corresponding vortex at the centre of the ω -rectangle is always stationary. The point $r = \sqrt{ab}$, $\theta = \frac{1}{2}\epsilon$, in the z -plane corresponds to the centre, C , in the ω -plane. Apparently Greenhill assumes that corresponding vortices in two conformally represented planes continue to move so as to occupy corresponding points. We easily see from (7) that in general this is not true.

⁹ *Loc. cit.*, 28,

In the present case the point at which the vortex is stationary is readily found from the condition

$$\frac{\partial X}{\partial r} = 0, \frac{\partial X}{\partial \theta} = 0$$

Using (11) we get

$$\beta = K', \text{ i.e., } \theta = \frac{1}{2}\epsilon,$$

and
$$1 + \frac{2K' \operatorname{Cn} a \operatorname{dn} a}{\epsilon \operatorname{Sn} a} = 0,$$

$$\text{i.e., } \frac{\operatorname{dn} 2a}{\operatorname{dn} 2a - \operatorname{Cn} 2a} = \frac{\epsilon^2}{4k'^2 K'^2},$$

or
$$\operatorname{Sn} (2a - K) = \operatorname{Sn} \left(\frac{4K'}{\epsilon} \log \frac{r}{a} - K \right) = \frac{4k'^2 K'^2 - \epsilon^2}{4k'^2 K'^2 + \frac{\epsilon^2}{2}}, \quad \dots \quad (22)$$

which determines r . We also have the relation

$$\frac{K}{K'} = \frac{\log (b/a)}{\epsilon}$$

To take a simple example we put $K = K' = 1.854$, $k = k' = 1/\sqrt{2}$, $a = 1$, $\epsilon = \frac{1}{2}\pi$. The value of b is $e^{\frac{1}{2}\pi} = 4.810$. From (22) we get

$$\operatorname{Sn} \left(\frac{8K}{\pi} \log r - K \right) = 0.472,$$

$$\text{i.e., } \log r = \frac{1}{8}\pi \left(1 + \frac{0.503}{K} \right) = 0.499$$

$$\text{or } r = 1.647.$$

Thus the point at which the vortex is stationary is given by $r = 1.647$, $\theta = \frac{1}{4}\pi$. According to Greenhill the value of r should be \sqrt{b} , i.e., 2.193.

When the rectangle is formed by arcs of co-axial circles we can take

$$\omega + (a_1 + i\beta_1) = -\mu \log \frac{z-a}{z+a} \quad \dots \quad \dots \quad (23)$$

so that the ω -rectangle is given by $a = 0$, $a = a_2 - a_1 = 2K$, $\beta = 0$, $\beta = \beta_2 - \beta_1 = 2K'$. Putting $z - a = r_1 e^{i\theta_1}$, $z + a = r_2 e^{i\theta_2}$, we get from (11)

$$-\frac{1}{r_1^2 r_2^2} \left[nS^2 \left\{ \left(\mu \log \frac{r_1}{r_2} + a_1, k \right) \right\} + nS^2 \{ \mu (\theta_1 - \theta_2) + \beta_1, k' \} - 1 \right] = \text{a constant} \quad \dots \quad (24)$$

as the curve described by the vortex.

In like manner when the sides are arcs of confocal conics we can get the corresponding results by using the relation

$$\omega + (a_1 + i\beta_1) = \sin^{-1} \frac{z}{c},$$

the ω -rectangle being the same as in the last example.

DIFFRACTION OF LIGHT BY ULTRASONIC WAVES.

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(Communicated by Sir C. V. Raman, Kt, F.R.S., N.L.)

Part I. Effect of Oblique Incidence.

IN a series of interesting papers, Sir C. V. Raman and N. S. Nagendra Nath¹ have developed a theory for the diffraction of light by high frequency sound waves, the essential idea being the diffraction of the corrugated form of the transmitted wave-front of light. Their theory has been able to explain many of the experimental results of R. Bär² and of Debye and Sears.³ In Part II of their theory they have very satisfactorily explained the curious phenomenon of the wandering of the intensities of the various orders observed first by Debye and Sears on tilting the trough containing the liquid. Their theory also explains the disappearance of the diffraction effects at greater angles of obliquity. The standpoint developed by them in Parts IV and V of their series, based on the wave-equation governing the propagation of light in a medium filled with sound waves explains the asymmetry in the diffraction pattern. In this paper the author presents detailed results of investigation with regard to the asymmetry observed in the diffraction spectra.

The asymmetry in the diffraction spectra was observed, simultaneously and independently by Lucas and Biquard,⁴ and by Debye and Sears in their earliest papers, and later by the author while carrying out determinations of ultrasonic velocities in various organic liquids. It has been recently investigated in detail by Bär⁵ also.

Results.

The experimental arrangement was the one followed earlier and described in previous papers.

It was found by the author that when the quartz crystal, set up to excite vibrations in the liquid, is inclined to the incident parallel beam, then an asymmetry in the diffraction spectra was observed.

Fig. 1 shows the arrangement. θ represents the angle through which the quartz plate Q is turned in the direction shown by the arrow, and is

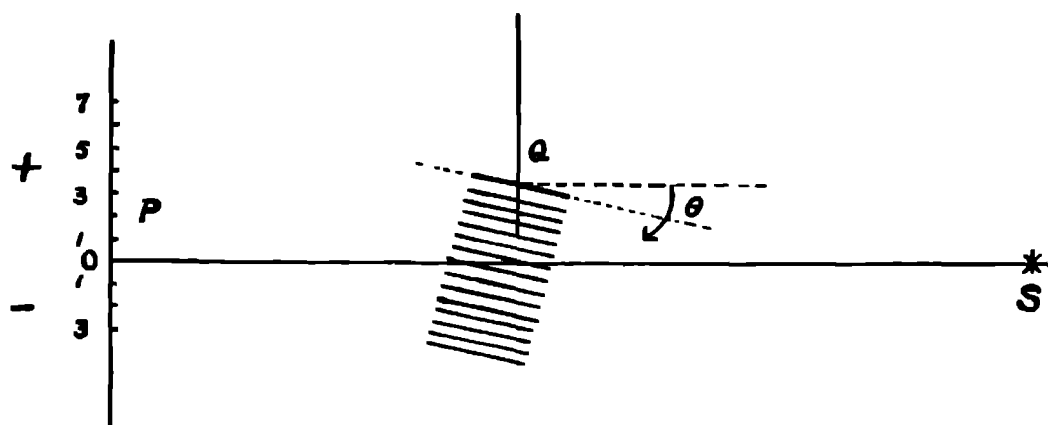


FIG. 1.

given in Fig. 2, in minutes of arc. *P* is the ground-glass plate on which are received the diffraction spectra. The upper portion is the right side (say +) where the greater number of orders is observed when the tilt is as shown in the diagram

It is necessary to make exact determinations of the angle of inclination for obtaining the relationship between the nature of asymmetry in the spectra and the angle of inclination. This can be useful to test further the theory relating to the diffraction spectra.

To the centre of the ebonite piece carrying the quartz crystal, of $20 \times 20 \times 2$ mms., a straight rigid steel rod of 310 mms. in length was firmly attached by sealing wax. The free-end of the rod, which was sharp and pointed, moved over a vertical scale, divided into millimeters, so that any small inclination could be read off accurately

A series of photographs of the spectra were taken at different inclinations of the quartz, with the parallel position marked zero. The frequency employed was 7.37×10^6 c/s., while only the spectra for 5461 \AA of the mercury arc were photographed.

We describe below, the positions, number and intensities of the different orders, as seen visually, at various angles of inclination. Fig. 2 bears this out amply. The intensities are not accurate but should be taken as indicative of the progress of changes accompanying the inclination.

The liquid, benzene, was contained in a tall vessel 12" high with plane plates serving as walls. Progressive waves were employed throughout.

For incident light parallel to the sound wave-front, the position indicated by 0 in the figure (Fig. 2), the number of orders is equal on either side, with symmetrical distribution of intensity. At a small angle of even $6'$, the fifth order on the right (say +) has begun to brighten up, almost double

in intensity, while it is evident that other orders on the same side are brighter than the corresponding ones on the left (say $-$) The $+1$ order is more intense than -1 , $+2$ more intense than -2 , and so on, each to each in the same spectrum. The difference in intensities, of $+3$ and -3 orders, for inclination marked $22'$, is remarkable.

The plate was slowly turned and kept at a position corresponding to the maximum number of orders that could be obtained on the $+$ side. The quartz plate has made an angle of $22'$. It should be remarked here that the total number of diffraction spectra remains what it was for symmetrical distribution, but with this difference, that the number and the intensity distribution are not the same as before. One could very easily see visually in the above experiment that the $+1$ order increases in intensity to a maximum and then falls gradually for increasing angle of the light beam to the sound wave-front. The displacement in the spectra corresponding to the maximum number of orders on the $+$ side, was two orders; that is, the $+$ side had increased by two, while the $-$ side had lost two. The pattern is asymmetrical.

On still further increasing the angle to $28'$, one could see that the asymmetry was maintained while progressively about the same number of orders disappeared from either side of the zero order. Even at such a large angle as $72'$, the $+2$ order is definitely more intense than the -2 order and it is only at $94'$ and greater angle that something like symmetry is brought about. At still greater angles, one sees only the first order spectrum getting fainter and fainter—so that finally at an inclination of 2° , even the first order has almost disappeared.

We give below the visual estimate of intensities for different orders at four inclinations only. The intensities are only relative but indicate the progressive changes accompanying the tilting of the quartz plate.

TABLE I.
Visual Estimate of Relative Intensities

Angle of Inclination	$-$ Order			$+$ Order			
	5	3	1	1	3	5	7
0	1	8	20	20	8	1	0
$6'$	$\frac{1}{2}$	6	20	25	12	2	0
$22'$	0	3	25	30	20	6	2
$28'$	0	1	6	15	8	1	less than $\frac{1}{2}$

An exactly similar set of changes occurred when the quartz plate was turned in the opposite direction, but now the greater number of orders was observed on the — side of the zero order, as against the + side as observed previously

Part II. A Case of Overlapping Resonance.

While the author was experimenting, he observed a curious phenomenon. At one stage in the setting of the variable condenser, he obtained one kind of diffraction spectra, and not far from it, not more than 40° in the setting of the variable condenser, another set of spectra, with distances for the first orders in the ratio 2 : 3. At some intermediate position between the two, the two first orders were obtained simultaneously on the ground-glass plate; while turning of the condenser either way, increased the intensity of one kind or the other, depending on the direction it was turned, with consequent diminution of the other kind. This was quite unexpected, and therefore the electrical wave-length for the two resonances were determined by means of a wave-meter, to determine the exact frequency with which the quartz was oscillating.

These frequencies were again checked in the following way. Since the liquid used was benzene, we know with fair accuracy the velocity of sound in it, and from a knowledge of the angles θ_1 and θ_2 which the first order of each kind produces, it is easy to calculate the wave-length of sound in the medium and hence the frequency of oscillation of the quartz plate.

The quartz plate used was of dimensions $20 \times 20 \times 1$ mms

The following table gives the results obtained in the case of overlapped resonance.

TABLE II.

No.	At the point of overlapping resonance			Frequency at the resonance point in c/s.	Number of the harmonic of the crystal
	Wave-length of sound in benzene in mms.	Frequency from previous column in c/s	Frequency by wave-meter reading in c/s.		
1	2.000 mms.	6.46×10^6	6.45×10^6	6.75×10^6	$5/2$ "
2	2.945 mms.	9.69×10^6	9.70×10^6	9.45×10^6	$7/2$ "

It is evident, therefore, that the crystal is vibrating at the $5/2$ th and $7/2$ th harmonic of the crystal, simultaneously.

We know that in liquids the resonances are broad and the present result is a case of superposition of the base of the two resonances, occurring

near to each other. This is clear if we closely notice what happens if the condenser is turned either way. Along the reading common to both, one of the spectra should get brighter depending upon the fact how much of the curve of the other it overlaps, and then finally should reach the pure resonance of $\frac{5}{2}n$ or $\frac{7}{2}n$ where n is the fundamental of the quartz. This was realised completely in the experiment.

Fig. 3 is a photograph of the overlapped resonance, while Fig. 4 gives the true graphical representation of facts.

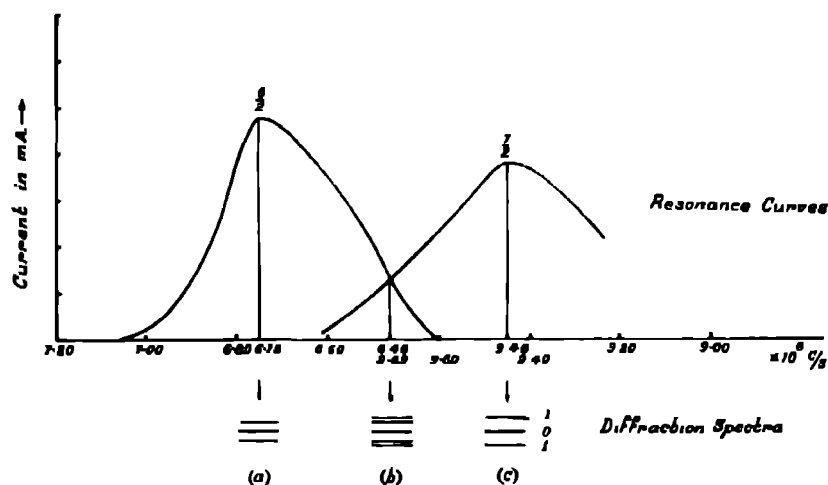


FIG. 4.

It will be worth recording here that L. Bergmann⁶ observed and proved by these optical methods, the simultaneous existence of fundamentals and harmonics, and any two harmonics, and it has not been known whether such $\frac{7}{2}n$ and $\frac{5}{2}n$ are possible of excitation. It is a fact known to all in the field of radio communication that transmitters are capable, in addition to the fundamental frequency, of sending harmonics, but always with the fundamental, though feebly.

Fig. 5 reproduces the diffraction spectra due to standing waves in *p*-Xylene at 7.32×10^6 c/s. Others have reported previously, notable among them being Oyama,^{7*} on the production of a large number of diffraction orders due to ultrasonic waves. The number of orders observed by the author is 16 and it will be interesting to account for such a large number and also their intensities by the Raman-Nath theory as developed in Part III. Further work is being continued in this direction.

The author thanks Professor Sir C. V. Raman for the interest he took in the work.

* Oyama's 30 orders really correspond to 15 orders; he probably means 30 lines, which will be $+15$ and -15 orders. Nobody seems to have obtained even as great many as 20 orders of diffraction spectra. 16 appears to be the maximum.

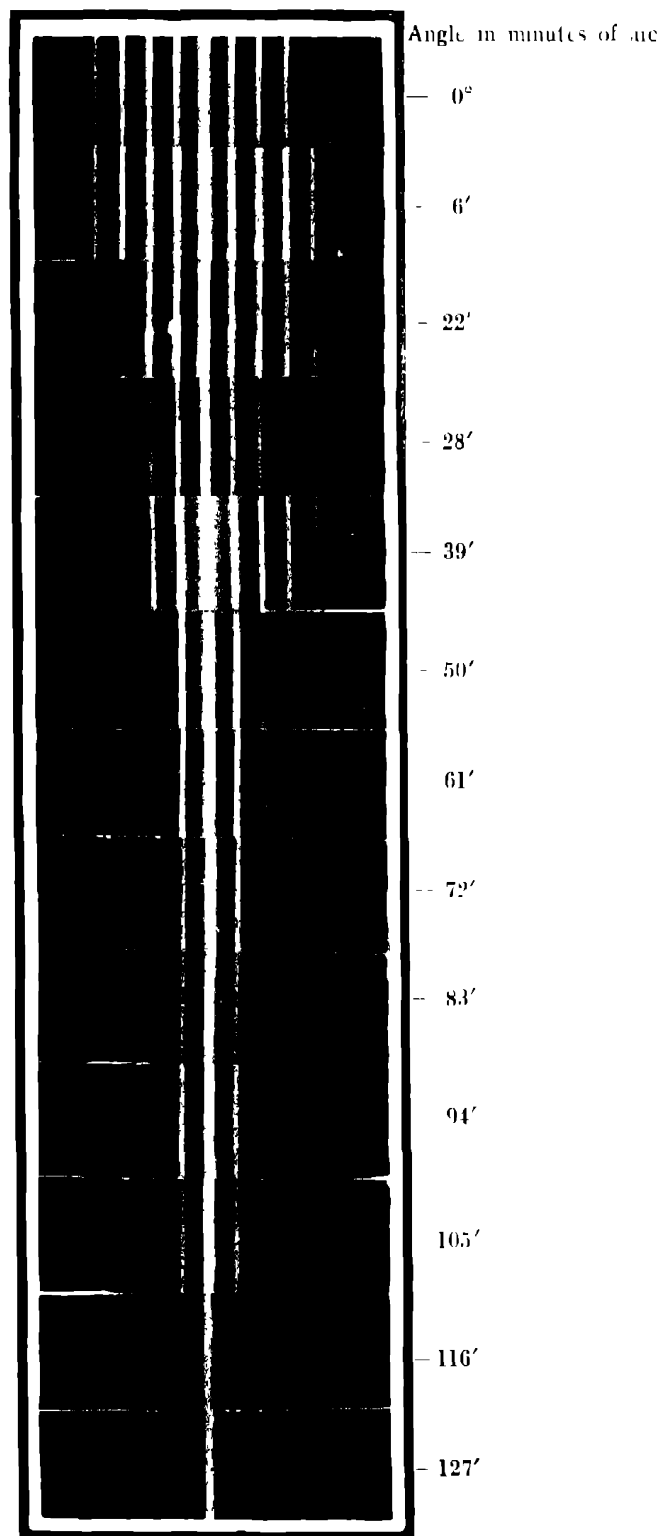


FIG. 2

Diffraction spectra at small angles between the incident light beam and the sound wave front

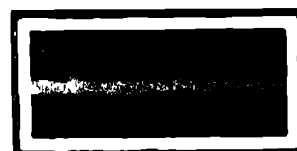


FIG. 3

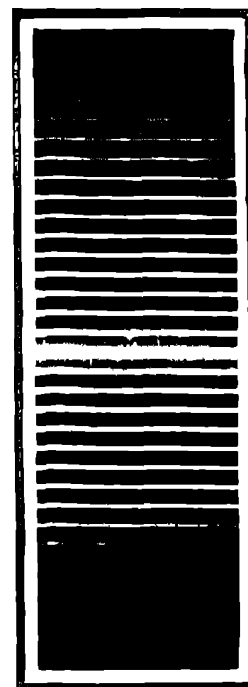


FIG. 5.

In *p* Xylene

Summary.

A detailed relationship between the angle of inclination of the oscillating quartz, and the diffraction spectra produced by it at these angles, is given. It is explicable on the basis of the Raman-Nath theory for the diffraction of light by high-frequency sound waves. The paper includes the case of overlapped resonance, the resonances occurring at $\frac{7}{2}n$ and $\frac{5}{2}n$, independent of each other.

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NEUTRINOS AND LIGHT QUANTA.*

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1. Introduction

JORDAN who has initiated the Neutrino Theory of light has indicated that optical phenomena are really simultaneous actions of pairs of neutrinos which obey the Fermi-Dirac statistics. His investigation is of very great significance for it shows that the only primary statistics in physical phenomena is the Fermi-Dirac one with anti-symmetric wave functions. He has shown that photons which obey the Bose-Einstein statistics do not really exist at all but that they constitute only a secondary effect appearing under special circumstances, that is, the way of the interaction of the neutrinos with electric charges leads to the effect that pairs of neutrinos behave generally as photons. Recently, a report was published in these *Proceedings* by Max Born and the author on the above work of Jordan and some developments in the same subject due to Kronig. We have removed therein many of the apparent contradictions involved in their papers. The chief one of them was with regard to the spin of the neutrino. We found that there was no reason to introduce the spin of the neutrino so far as the up-to-date results of Jordan and Kronig were concerned. We had only to postulate only one kind of neutrino with positive or negative energy. That is, there was no need to distinguish between the two kinds of neutrinos for they differ in the same way as electrons and positrons in Dirac's theory of holes. The spin is a property independent of this distinction which has to be introduced separately and will be treated in this paper. The difficulties regarding the negative infinite energy were removed by introducing the idea of holes for the variables of the states as is done in Dirac's theory of holes. We also pointed out that the way of the interaction of the neutrinos with electrons could be simply formulated in the one principle that the average photon energy density of energy l is given as a Raman effect with the universal rule: Absorption of a neutrino of any (positive or negative) energy κ and the simultaneous emission of a neutrino with the energy $\kappa - l$ where $-\infty < \kappa < \infty$.

* The writing up of this paper is on similar lines as to be found in the report by Max Born and the author, *Proc. Ind Acad Sci.*, 1936, 3, 318. The above report is referred to in this paper as BN. References to the literature are to be found there.

It is quite definite that the idea of spin is unnecessary so far as the present Jordan-Kronig results are concerned. But the existence of the spin cannot be rejected if we examine the problem more carefully. One of the primary reasons for the existence of the spin for the neutrino is that it obeys the Fermi-Dirac statistics. Secondly, if we wish to retain the idea that the total spin is conserved in the processes of the interaction between neutrinos and electrons (or other elementary particles), we would be unable to understand the change in the spin of an electron in electron transitions influenced by the presence of the neutrinos if that change of spin does not arise from the neutrinos. In the case of electrons in atoms, we should also remember the change in the angular momentum of an atom during such processes. Born opines that a satisfying theory including the above point could only be developed by a proper treatment of the problem in three dimensions. Apart from all these reasons, there is still another vital reason to introduce the spin for the neutrino. It is that we will have to incorporate in the theory of light, the idea of polarisation and derive the Planck formula for the radiation density. The former point is as yet untouched by previous investigators while the latter point has been dealt with by Jordan but not with complete success. *Jordan's expression for the radiation density is only half of Planck's formula for Jordan's photons have no polarisation properties.* In the following paper these difficulties have been removed by a proper treatment of the spin of the neutrino.

It is the purpose of this paper to introduce the spin of the neutrino and to show that we get two different photon operators for photons with the same energy and thus obtain the Planck formula for the density of radiation.

2. Neutrino Operators and their Jordan-Wigner Representations

Two infinite sets of non-commuting variables $a_{\kappa,i}$, $\gamma_{\kappa,i}$ are chosen as the operators describing the neutrinos, where κ takes all the positive half integral numbers $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ and i takes the only two values R and L, which characterise the two spin states. We introduce operators with negative indices defined as follows:—

$$(1) \quad a_{-\kappa,i} = \gamma_{\kappa,i}^\dagger; \quad \gamma_{-\kappa,i} = a_{\kappa,i}^\dagger \quad \kappa > 0.$$

The above operators obey the following commutation rules.

$$(2) \quad \begin{aligned} a_{\kappa,i} a_{\mu,j} + a_{\mu,j} a_{\kappa,i} &= 0 \\ \gamma_{\kappa,i} \gamma_{\mu,j} + \gamma_{\mu,j} \gamma_{\kappa,i} &= 0 \\ \gamma_{\kappa,i} a_{\mu,j} + a_{\mu,j} \gamma_{\kappa,i} &= \delta_{\mu,-\kappa} \delta_{i,j}. \end{aligned}$$

The operators describing the number of neutrinos and anti-neutrinos of energy κ , ($\kappa > 0$) are defined by the following operators.

$$(3) \quad \begin{aligned} N_{\kappa,i}^{(+)} &= a_{\kappa,i}^\dagger a_{\kappa,i} = 1 - a_{\kappa,i} a_{\kappa,i}^\dagger \\ N_{\kappa,i}^{(-)} &= \gamma_{\kappa,i}^\dagger \gamma_{\kappa,i} = 1 - \gamma_{\kappa,i} \gamma_{\kappa,i}^\dagger \end{aligned}$$

As in BN, we can write down the Jordan-Wigner representation of the neutrino operators by the following scheme.

(4) $\kappa > 0$	$\frac{1}{2}, R$; $\frac{1}{2}, L$; $-\frac{1}{2}, R$; $-\frac{1}{2}, L$; ---- ; κ, R ; κ, L ; $-\kappa, R$; $-\kappa, L$; ----
$a_{\kappa, R} = \gamma_{-\kappa, R}^\dagger$	s \times s \times s \times s \times \times ---- \times a \times 1 \times 1 \times \times ----
$a_{\kappa, L} = \gamma_{-\kappa, L}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times a \times 1 \times 1 \times ----
$a_{-\kappa, R} = \gamma_{\kappa, R}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times s \times a^\dagger \times 1 \times ----
$a_{-\kappa, L} = \gamma_{\kappa, L}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times s \times s \times a^\dagger \times ----
$\gamma_{\kappa, R} = a_{-\kappa, R}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times s \times a \times 1 \times ----
$\gamma_{\kappa, L} = a_{-\kappa, L}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times s \times s \times a \times ----
$\gamma_{-\kappa, R} = a_{\kappa, R}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times a^\dagger \times 1 \times 1 \times ----
$\gamma_{-\kappa, L} = a_{\kappa, L}^\dagger$	s \times s \times s \times s \times \times ---- \times s \times s \times a^\dagger \times 1 \times 1 \times ----

where

$$(5) \quad a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \quad s = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and the sign of multiplication refers to the symbol of direct product of matrices defined in BN.

Each matrix has only one non-vanishing element given by the following scheme in which $t_{\kappa,i}$ is zero or unity.

(6)

$$\begin{aligned}
 a_{\kappa,R} & \left(---, 0, t_{\kappa,L}, t_{-\kappa,R}, t_{-\kappa,L}, ---; ---, 1, t_{\kappa,L}, t_{-\kappa,R}, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{-(\kappa-1),L}} \\
 a_{\kappa,L} & \left(---, t_{\kappa,R}, 0, t_{-\kappa,R}, t_{-\kappa,L}, ---; ---, t_{\kappa,R}, 1, t_{-\kappa,R}, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{\kappa,R}} \\
 a_{-\kappa,R} & \left(---, t_{\kappa,R}, t_{\kappa,L}, 1, t_{-\kappa,L}, ---; ---, t_{\kappa,R}, t_{\kappa,L}, 0, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{\kappa,L}} \\
 a_{-\kappa,L} & \left(---, t_{\kappa,R}, t_{\kappa,L}, t_{-\kappa,R}, 1, ---; ---, t_{\kappa,R}, t_{\kappa,L}, t_{-\kappa,R}, 0, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{-\kappa,R}} \\
 \gamma_{\kappa,R} & \left(---, t_{\kappa,R}, t_{\kappa,L}, 0, t_{-\kappa,L}, ---; ---, t_{\kappa,R}, t_{\kappa,L}, 1, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{\kappa,L}} \\
 \gamma_{\kappa,L} & \left(---, t_{\kappa,R}, t_{\kappa,L}, t_{-\kappa,R}, 0, ---; ---, t_{\kappa,R}, t_{\kappa,L}, t_{-\kappa,R}, 1, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{-\kappa,R}} \\
 \gamma_{-\kappa,R} & \left(---, 1, t_{\kappa,L}, t_{-\kappa,R}, t_{-\kappa,L}, ---; ---, 0, t_{\kappa,L}, t_{-\kappa,R}, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{-(\kappa-1),L}} \\
 \gamma_{-\kappa,L} & \left(---, t_{\kappa,R}, 1, t_{-\kappa,R}, t_{-\kappa,L}, ---; ---, t_{\kappa,R}, 0, t_{-\kappa,R}, t_{-\kappa,L}, --- \right) \\
 & = (-)^{t_{\frac{1}{2},R} + --- + t_{\kappa,R}}
 \end{aligned}$$

3. A New System of Operators

As in BN, we introduce operators $a_{\kappa,i}$ and $c_{\kappa,i}$ defined by

$$\begin{aligned}
 (7)^* \quad a_{\kappa,i} & = \frac{a_{\kappa,i} + \gamma_{\kappa,i}}{\sqrt{2}}; \\
 c_{\kappa,i} & = \frac{a_{\kappa,i} - \gamma_{\kappa,i}}{i\sqrt{2}}.
 \end{aligned}$$

We can express $a_{\kappa,i}$ and $\gamma_{\kappa,i}$ as functions of $a_{\kappa,i}$ and $c_{\kappa,i}$ as

$$\begin{aligned}
 (8) \quad a_{\kappa,i} & = \frac{a_{\kappa,i} + i c_{\kappa,i}}{\sqrt{2}}; \\
 \gamma_{\kappa,i} & = \frac{a_{\kappa,i} - i c_{\kappa,i}}{\sqrt{2}}.
 \end{aligned}$$

It can be easily found from (7) and (1) that

$$(9) \quad a_{-\kappa,i} = a_{\kappa,i}^\dagger; \quad c_{-\kappa,i} = c_{\kappa,i}^\dagger.$$

*No confusion should be made in i which characterises the spin states occurring in the suffixes and which denotes $\sqrt{-1}$ otherwise.

Also, a 's and c 's can be seen to obey the following commutation rules with the help of (2) and (8).

$$(10) \quad \begin{aligned} a_{\kappa,i} a_{\mu,j} + a_{\mu,j} a_{\kappa,i} &= \delta_{\mu,-\kappa} \delta_{i,j} \\ c_{\kappa,i} c_{\mu,j} + c_{\mu,j} c_{\kappa,i} &= \delta_{\mu,-\kappa} \delta_{i,j} \\ a_{\kappa,i} c_{\mu,j} + c_{\mu,j} a_{\kappa,i} &= 0 \end{aligned}$$

for $\kappa, \mu = \pm \frac{1}{2}, \pm \frac{3}{2}, \dots$ and $i, j = R, L$.

We define the operators $L_{\kappa,i}$ and $N_{\kappa,i}$ to be given by

$$(11) \quad L_{\kappa,i} = a_{\kappa,i}^\dagger a_{\kappa,i}; \quad N_{\kappa,i} = c_{\kappa,i}^\dagger c_{\kappa,i}.$$

It will be quite easy to see that

$$(12) \quad \begin{aligned} L_{\kappa,i} + N_{\kappa,i} &= N_{\kappa,i}^{(+)} + N_{\kappa,i}^{(-)}, \\ L_{\kappa,i} - N_{\kappa,i} &= a_{\kappa,i}^\dagger \gamma_{\kappa,i} + \gamma_{\kappa,i}^\dagger a_{\kappa,i}. \end{aligned}$$

Under the same considerations as in BN, we can show that

$$(13) \quad \sum L_{\kappa,i} \quad \text{and} \quad \sum N_{\kappa,i}$$

are convergent.

4 The Operators describing the Photon States.

For each energy state k we introduce two operators defined by

$$(14a) \quad b_{k,\rho} = \frac{1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum' a_{\kappa,i} c_{k-\kappa,i}$$

and

$$(14b) \quad b_{k,\lambda} = \frac{1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum' a_{\kappa,i} c_{k-\kappa,i}$$

for $k = \pm 1, \pm 2, \pm 3, \dots$, where the dash over the (i, j) summation sign indicates that $i \neq j$.

It may be easily found that

$$(15) \quad b_{k,i}^\dagger = b_{-k,i} \quad \text{where } i = \rho, \lambda.$$

We can find expressions for these new operators in terms of a 's and γ 's. They are

$$(16) \quad \begin{aligned} b_{k,\rho} &= \frac{-1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum' a_{\kappa,i} \gamma_{k-\kappa,i} \\ b_{k,\lambda} &= \frac{-1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum' a_{\kappa,i} \gamma_{k-\kappa,i} \end{aligned}$$

We also introduce two operators B_ρ and B_λ defined by

$$(17) \quad \begin{aligned} B_\rho &= \frac{i}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum a_{\kappa,i} c_{-\kappa,i} = \frac{1}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum (a_{\kappa,i}^\dagger a_{\kappa,i} - \gamma_{\kappa,i}^\dagger \gamma_{\kappa,i}) \\ B_\lambda &= \frac{i}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j} \sum' a_{\kappa,i} c_{-\kappa,j} = \frac{1}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j} \sum' (a_{\kappa,i}^\dagger a_{\kappa,j} - \gamma_{\kappa,i}^\dagger \gamma_{\kappa,j}) \end{aligned}$$

We will now examine the commutability of these operators defined by (14) and (10) *

$$\begin{aligned} (a) \quad [b_{r,\rho}, b_{s,\rho}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_{u,v} (a_{m,u} c_{s-m,u} a_{l,v} c_{r-l,v} \\ &\quad - a_{l,v} c_{r-l,v} a_{m,u} c_{s-m,u}) \\ &= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_u (a_{l,u} a_{-l+r+s,u} - c_{l+s,u} c_{r-l,u}) \\ &= 0 \text{ if } r+s \neq 0, \\ &= 1 \text{ if } r+s=0, \quad r>0. \\ (b) \quad [b_{r,\lambda}, b_{s,\lambda}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_{u,v} \sum_{i,j}' (a_{m,u} c_{s-m,v} a_{l,i} c_{r-l,j} \\ &\quad - a_{l,i} c_{r-l,j} a_{m,u} c_{s-m,v}) \\ &= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_i (a_{l,i} a_{-l+r+s,i} - c_{s+l,i} c_{r-l,i}) \\ &= 0 \text{ if } r+s \neq 0, \\ &= 1 \text{ if } r+s=0, \quad r>0. \\ (c) \quad [b_{r,\rho}, b_{s,\lambda}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_i \sum_{u,v}' (a_{m,u} c_{s-m,v} a_{l,i} c_{r-l,i} \\ &\quad - a_{l,i} c_{r-l,i} a_{m,u} c_{s-m,v}) \\ &= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_{i,j}' (a_{l,i} a_{-l+j+s,j} - c_{s+l,i} c_{r-l,j}) \\ &= 0 \\ (d) \quad [B_\lambda, b_{r,\lambda}] &= \frac{1}{2\sqrt{|r|}} \sum_{l,m} \sum_{i,j} \sum_{u,v}' (a_{m,u} c_{r-m,v} a_{l,i} c_{-l,j} \\ &\quad - a_{l,i} c_{-l,j} a_{m,u} c_{r-m,v}) \\ &= \frac{1}{2\sqrt{|r|}} \sum_l \sum_{i,j}' (a_{l,i} a_{r-l,j} - c_{r+l,i} c_{-l,j}) \\ &= 0 \\ (e) \quad [B_\rho, b_{r,\lambda}] &= \frac{1}{2\sqrt{|r|}} \sum_{l,m} \sum_i \sum_{u,v}' (a_{m,u} c_{r-m,v} a_{l,i} c_{-l,i} \\ &\quad - a_{l,i} c_{-l,i} a_{m,u} c_{r-m,v}) \\ &= 0 \end{aligned}$$

* As in BN, we assume that the series

$$\sum a_{-\kappa+r,i} a_{\kappa,i} \text{ and } \sum c_{-\kappa+r,i} c_{\kappa,i}$$

are convergent for any finite r . Refer BN for further details.

$$(f) [B_\lambda, b_{r,\rho}] = 0$$

$$(g) [B_\rho, b_{r,\rho}] = 0$$

$$(h) [B_\rho, B_\lambda] = 0$$

Thus

$$(18) \quad \begin{array}{l} b_{r,\iota} b_{s,\sigma} - b_{s,\sigma} b_{r,\iota} = \delta_{r,-s} \delta_{\iota,\sigma} \\ B_\iota b_{r,\sigma} - b_{r,\sigma} B_\iota = 0 \\ B_\rho B_\lambda - B_\lambda B_\rho = 0 \end{array}$$

for $\iota, \sigma = \rho, \lambda$ and $r > 0$.

5 Photons and Statistical Equilibrium

The photons in a hohlraum can be represented by a set of variables $b_{k,\iota}$ which satisfy the commutation rules (18). For a state with given number of neutrinos $N^{(+)}$ and $N^{(-)}$ the operators representing the number of photons in the k th energy state with the indices ρ, λ are

$$(19) \quad P_{k,\rho} = b_{k,\rho}^\dagger b_{k,\rho}; \quad P_{k,\lambda} = b_{k,\lambda}^\dagger b_{k,\lambda}.$$

The average value of the number of photons with energy k is

$$(20) \quad \begin{aligned} \bar{P}_k &= \bar{P}_{k,\rho} + \bar{P}_{k,\lambda} \\ &= \sum_{\iota_{\frac{1}{2},R}, \iota'_{\frac{1}{2},L}, \iota'_{-\frac{1}{2},R}, \iota'_{-\frac{1}{2},L}} \left\{ |b_{k,\rho}(\iota_{\frac{1}{2},R}, ---; \iota'_{\frac{1}{2},R}, ---)|^2 \right. \\ &\quad \left. + |b_{k,\lambda}(\iota_{\frac{1}{2},R}, ---; \iota'_{\frac{1}{2},R}, ---)|^2 \right\} \end{aligned}$$

Just as in BN, we can show that

$$(21) \quad \begin{aligned} \bar{P}_k &= \frac{1}{2k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} \sum_i N_{\kappa,i}^{(+)} N_{k-\kappa,i}^{(-)} + \frac{1}{2k} \sum_{\frac{1}{2}}^{\infty} \sum_i \{N_{k+\kappa,i}^{(+)} (1 - N_{\kappa,i}^{(+)}) \\ &\quad + N_{k+\kappa,i}^{(-)} (1 - N_{\kappa,i}^{(-)})\} \\ &\quad + \frac{1}{2k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} \sum_{i,j} N_{\kappa,i}^{(+)} N_{k-\kappa,j}^{(-)} + \frac{1}{2k} \sum_{\frac{1}{2}}^{\infty} \sum_{i,j} \{N_{k+\kappa,i}^{(+)} (1 - N_{\kappa,i}^{(+)}) \\ &\quad + N_{k+\kappa,i}^{(-)} (1 - N_{\kappa,i}^{(-)})\} \end{aligned}$$

We will now assume that the average number of neutrinos of energy κ in the R state is equal to the average number of neutrinos of energy κ in the L state. Thus

$$(22) \quad \begin{aligned} N_{\kappa,R}^{(+)} &= N_{\kappa,L}^{(+)} = N_{\kappa}^{(+)}; \\ N_{\kappa,R}^{(-)} &= N_{\kappa,L}^{(-)} = N_{\kappa}^{(-)}, \end{aligned}$$

so that

$$(23) \quad \begin{aligned} \bar{P}_k &= \frac{2}{k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} N_{\kappa}^{(+)} N_{k-\kappa}^{(-)} + \frac{2}{k} \sum_{\frac{1}{2}}^{\infty} \{N_{k+\kappa}^{(+)} (1 - N_{\kappa}^{(+)}) \\ &\quad + N_{k+\kappa}^{(-)} (1 - N_{\kappa}^{(-)})\}. \end{aligned}$$

We can show that

$$(24) \quad N_i^{(+)} = \frac{ay}{1+ay} \text{ and } N_i^{(-)} = \frac{y/a}{1+y/a}$$

where $y = e^{-\beta'}$ and $\beta = h\nu_1/kT$.

Following the same procedure as in BN, we find

$$(25) \quad \overline{P}(\nu) = \frac{2}{e^{h\nu/kT} - 1}.$$

If we assume that the density of radiation with frequency lying between ν and $\nu + d\nu$ is

$$(26) \quad \frac{4\pi\nu^2 d\nu}{c^3} h\nu (\overline{P}_{r,\rho} + \overline{P}_{r,\lambda}), \quad r\nu_1 = \nu$$

we get the density of radiation to be*

$$(27) \quad \frac{4\pi\nu^2 d\nu}{c^3} h\nu \overline{P}(\nu) = \frac{8\pi\nu^2 d\nu}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

which is the Planck formula for the radiation density

6 Jordan's Derivation of the Formula for the Radiation Density.

According to Jordan

$$\overline{P}(\nu) = \frac{1}{e^{h\nu/kT} - 1}.$$

The number of radiation oscillators per unit volume is

$$\frac{4\pi\nu^2 d\nu}{c^3}$$

as the photons defined by Jordan have no polarisation properties. Therefore, Jordan has effectively got only half of Planck's formula. Even if we restrict our considerations to one dimensional hohlraum this difficulty does not disappear.

7 Relation between the Energy of Neutrinos and Photons

The energy of photons (in units of $h\nu_1$, ν_1 being the fundamental frequency of the hohlraum) is given by

$$(28) \quad \begin{aligned} W &= W_\rho + W_\lambda \\ &= \sum_k k (P_{k,\rho} + P_{k,\lambda}) \end{aligned}$$

* In three dimensions, we assume that (25) is the same for all the states with frequency ν .

The energy of neutrinos in the same units is given by

$$(29) \quad E = E_R + E_L \\ = \sum_k \sum_i k (L_{k,i} + N_{k,i}), \quad i = R, L.$$

$$W_\rho = -\frac{1}{2} \sum_{l,m}^{\infty} \sum_{i,u}^{\infty} \sum_k^{\infty} a_{l,i} c_{-k-l,i} a_{m,u} c_{k-m,u} \\ (30) \quad = \frac{1}{2} \sum_{l,m}^{\infty} \sum_k^{\infty} \sum_{i,j}^{\infty} a_{l,i} a_{m,j} c_{-k-l,i} c_{k-m,j} + \frac{1}{2} \sum_{l,i}^{\infty} \sum_k^{\infty} \sum_j^{\infty} a_{l,i} a_{-l,i} c_{-k-l,i} c_{k+l,i}$$

where the double dashes over the (l, m) and (i, j) summations indicate that $l \neq -m$ and $i \neq j$ simultaneously. Changing in the first summation k to $-k$, l to m , m to l , i to j , j to i and using the commutation rules (10), we get

$$(31) \quad W_\rho = \frac{1}{2} \sum_{l,m}^{\infty} \sum_k^{\infty} \sum_{i,j}^{\infty} a_{l,i} a_{m,j} c_{-k-l,i} c_{k-m,j} + \frac{1}{2} \sum_{l,i}^{\infty} \sum_k^{\infty} \sum_j^{\infty} a_{l,i} a_{-l,i} c_{-k-l,i} c_{k+l,i}$$

But

$$(32) \quad B_\rho^2 = \frac{1}{2} \sum_{l,m}^{\infty} \sum_{i,j}^{\infty} a_{l,i} a_{m,j} c_{-l,i} c_{-m,j} + \frac{1}{2} \sum_{l,i}^{\infty} \sum_j^{\infty} a_{l,i} a_{-l,i} c_{-l,i} c_{l,i}$$

Adding (30), (31) and (32), we get

$$(33) \quad 2W_\rho + B_\rho^2 = \frac{1}{2} \sum_{l,m}^{\infty} \sum_k^{\infty} \sum_{i,j}^{\infty} a_{l,i} a_{m,j} c_{-k-l,i} c_{k-m,j} \\ + \sum_{l,i}^{\infty} \sum_k^{\infty} \sum_j^{\infty} a_{l,i} a_{-l,i} c_{-k-l,i} c_{k+l,i} + \frac{1}{2} \sum_{l,i}^{\infty} \sum_j^{\infty} a_{l,i} a_{-l,i} c_{-l,i} c_{l,i}$$

Similarly

$$(34) \quad 2W_\lambda + B_\lambda^2 = \frac{1}{2} \sum_{l,m}^{\infty} \sum_k^{\infty} \sum_{i,j}^{\infty} \sum_{u,v}^{\infty} a_{l,i} a_{m,j} c_{-k-l,u} c_{k-m,v} \\ + \sum_{l,i}^{\infty} \sum_{j}^{\infty} \sum_k^{\infty} a_{l,i} a_{-l,i} c_{-k-l,i} c_{k+l,i} \\ + \frac{1}{2} \sum_{l,i}^{\infty} \sum_{j}^{\infty} a_{l,i} a_{-l,i} c_{-l,i} c_{l,i}$$

where the star over the (u, v) summation indicates that $i \neq u$ and $j \neq v$. Thus, adding (33) and (34), we get

$$2(W_\rho + W_\lambda) + (B_\rho^2 + B_\lambda^2) \\ = \frac{1}{2} \sum_{l,m}^{\infty} \sum_k^{\infty} \sum_{i,j}^{\infty} \sum_{u,v}^{\infty} a_{l,i} a_{m,j} (c_{-k-l,i} c_{k-m,j} + c_{-k-l,u} c_{k-m,v})$$

$$(35) \quad + \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} \sum_{i,j} \Sigma' a_{l,i} a_{-l,i} (c_{-k-l,i} c_{k+l,i} + c_{-k-l,j} c_{k+l,j})$$

$$+ \sum_{l=-\infty}^{\infty} \sum_{i,j} \Sigma' a_{l,i} a_{-l,i} (c_{-l,i} c_{l,i} + c_{-l,j} c_{l,j}).$$

In the first summation, if we add the k th term to $(-k-l+m)$ th term we get zero. Therefore, the whole sum is zero.

$$\therefore 2(W_\rho + W_\lambda) + B_\rho^2 + B_\lambda^2$$

$$= \sum_{l=-\infty}^{\infty} \sum_{k=1}^{\infty} \sum_{i,j} \Sigma a_{l,i} a_{-l,i} c_{-k-l,i} c_{k+l,i}$$

$$+ \frac{1}{2} \sum_{l=-\infty}^{\infty} \sum_{i,j} \Sigma a_{l,i} a_{-l,i} c_{-l,i} c_{l,i}$$

$$= \sum_{\frac{1}{2}}^{\infty} \sum_{i,j} \Sigma (1 - I_{l,i}) \sum_{k=1}^{\infty} \Sigma N_{k+l,i} + \sum_{\frac{3}{2}}^{\infty} \sum_{i,j} \Sigma I_{l,i} \sum_{k=1}^{l-\frac{1}{2}} \Sigma (1 - N_{k+l,i})$$

$$+ \sum_{\frac{3}{2}}^{\infty} \sum_{i,j} \Sigma I_{l,i} \sum_{k=1}^{\infty} \Sigma N_{k-l,i} + \sum_{l+\frac{1}{2}} \Sigma I_{\frac{1}{2},i} \sum_{k=1}^{\infty} \Sigma N_{k-\frac{1}{2},i}$$

$$+ \frac{1}{2} \sum_{\frac{1}{2}}^{\infty} \sum_{i,j} \Sigma (1 - I_{l,i}) \Sigma N_{l,i} + \frac{1}{2} \sum_{\frac{1}{2}}^{\infty} \sum_{i,j} \Sigma I_{l,i} \Sigma (1 - N_{l,i})$$

$$(36) \quad = 2 \sum_{\frac{1}{2}}^{\infty} \Sigma l (I_{l,i} + N_{l,i}) = 2 (E_R + E_L)$$

Thus

$$(37a) \quad \boxed{2(W_\rho + W_\lambda) + (B_\rho^2 + B_\lambda^2) = 2(E_R + E_L)}$$

$$(37b) \quad \therefore$$

$$\boxed{E - W = \frac{B_\rho^2 + B_\lambda^2}{2}}$$

A pure photon state would correspond to

$$B_\rho = 0; \quad B_\lambda = 0.$$

A pure neutrino state would correspond to

$$W = 0.$$

† It should be remembered that the energy is expressed in units of $\hbar \nu_1$.

7. Conclusion.

It is found necessary in this paper to introduce the spin of the neutrino in the neutrino theory of light in order to obtain two photon operators for each energy state of photons and derive the Planck formula. The derivation by Jordan without the idea of spin for the neutrino is not free from objection for he obtains half the Planck formula for the radiation density for his photons have no polarisation states. This difficulty disappears in our derivation of the Planck formula for we obtain two photon operators for each energy state of photons. These two operators are connected with the polarisation states of light.

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THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES : PART V.

General Considerations—Oblique Incidence and Amplitude Changes.

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1. Introduction.

THE essential idea that the phenomenon of the diffraction of light by high frequency sound waves depends on the corrugated form of the wave-front of the transmitted light has been pointed out by us in Part I of this series of papers¹. Therein, we considered that the corrugated wave-front of light could be simply obtained by considering the phase changes accompanying the traversing beam which was assumed to undergo no amplitude changes at its various points. This course was adopted by us to bring out the essential features of the theory without unnecessary complications. By a close study of the problem, one can however easily see that the consideration of the phase changes is far more important than the amplitude changes if we desire to understand the essential features of the phenomenon. Indeed, this fact holds if we consider the case when the sound wave field is small and the wave-length of sound is large. This has been experimentally confirmed quite recently by Bär.²

In Part IV of this series of papers, we proposed the method of obtaining the wave function of light by considering the partial differential equation governing the propagation of light in a medium filled with sound waves. *Such a procedure would naturally take account of both the amplitude changes and the phase changes accompanying the beam.* These changes should be however periodic in character. On these considerations we found that, in the case of a progressive sound wave, the n th order diffraction component will be inclined at an angle $\sin^{-1}(-n\lambda/\lambda^*)$ to the direction of propagation of the incident light and will have the frequency $\nu - n\nu^*$ where ν and λ denote the frequency and the wave-length of the incident light while ν^* and λ^* correspond to those of the sound wave. We also showed that when the disturbance in the medium is simple harmonic, the relative intensity of the

n th order is given by $|\phi_n|^2$ where ϕ_n is the solution of the equation

$$(1) \quad \mu^2 \frac{d^2 \phi_n}{d\xi^2} - 2i\mu_0\mu \frac{d\phi_n}{d\xi} - \frac{n^2\lambda^2}{\lambda^{*2}} \phi_n = -\mu_0\mu i (\phi_{n-1} - \phi_{n+1})$$

where $\xi = 2\pi\mu z/\lambda$, μ_0 is the refractive index of the undisturbed medium, μ is the amplitude of the variation of the refractive index and the z -axis is along the direction of propagation of the incident light. As μ is of the order 10^{-5} and μ_0 is of the order of unity, we could consider the equation for ϕ_n as given by

$$(2) \quad 2 \frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = \frac{in^2\lambda^2}{\mu_0\mu\lambda^{*2}} \phi_n$$

In the case of a stationary sound wave, we obtained the result that, in any even order, radiations with frequencies $\nu \pm 2\nu^*$ would be present, while in any odd order, radiations with frequencies $\nu \pm \overline{2r+1}\nu^*$ would be present. These results interpret the experimental results of Bar² regarding the coherence phenomena among the diffracted orders. If the disturbance in the medium is simple harmonic, we obtained the result that the amplitudes of the various components of the n th order are given by the Fourier analysis of $g_n(\xi, t)$ which satisfies the equation

$$(3) \quad 2 \frac{\partial g_n}{\partial \xi} - \sin \epsilon (g_{n-1} - g_{n+1}) = \frac{in^2\lambda^2}{\mu_0\mu\lambda^{*2}} g_n$$

where $\epsilon = 2\pi\nu^* t$ and the term containing the second derivative of g_n is omitted as its coefficient is very small. If one however ignores the spectral character of each order, then the relative intensity of the n th order is given by

$$(4) \quad \int_0^{2\pi} |g_n(\xi, \epsilon)|^2 d\epsilon.$$

These results pertain to the case of the incident light falling normally on the sound waves. One of the purposes of this paper is to extend the above considerations to the case of the oblique incidence of light to the sound waves. We have found that, in the case of oblique incidence, the intensity of the n th order need not be equal to that of the $-n$ th order, thus explaining the results of Debye and Sears,³ Lucas and Biqard,⁴ Bar and Parthasarathy.⁵ We have also investigated the amplitude changes accompanying the traversing wave-front explaining the results of Hiedemann,⁷ Bär⁸ and Lucas.⁶

2. The Diffraction of Light when it is Incident Obliquely to the Sound Waves.

We choose the axes of reference such that the x -axis points to the direction of propagation of the sound waves and the z -axis lies in the plane contained by the directions of propagation of the sound and the incident light waves. With the same considerations as in Part IV, the wave function of the light traversing the medium is given by

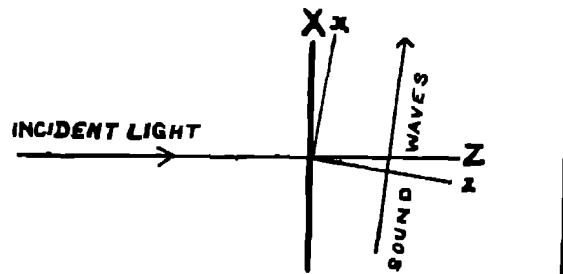


FIG. 1.

$$(5) \quad \psi = \exp(2\pi i \nu t) \Phi(x, z, t),$$

where Φ satisfies the equation

$$(6) \quad \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \{\mu(x, t)\}^2 \Phi.$$

Let $\cos \phi$ and $\sin \phi$ be the z - and x -direction cosines of the direction of propagation of the incident light. The transmitted wave travelling in the medium will suffer periodic fluctuations in its phase and amplitude with the period $\lambda^* \sec \phi$ along the line in the incident plane of light and the xz plane. Thus,

$$(7) \quad \Phi(x, z, t) = \Phi(x + p\lambda^*, z - p\lambda^* \tan \phi, t).$$

So, the wave travelling in the medium is given by

$$(8) \quad e^{2\pi i \nu t} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{rs} (x \sin \phi + z \cos \phi) e^{2\pi i r (x \cos \phi - z \sin \phi) / \lambda^* \sec \phi} e^{2\pi i s \nu^* t}$$

We choose a new axis of reference defined by

$$(9) \quad \begin{aligned} X &= x \cos \phi - z \sin \phi \\ Z &= x \sin \phi + z \cos \phi \end{aligned}$$

The new Z -axis is along the direction of propagation of the incident light. In the new system of reference, the wave function has to be written as

$$(10) \quad e^{2\pi i \nu t} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{rs} (Z) e^{2\pi i r X \cos \phi / \lambda^*} e^{2\pi i s \nu^* t}$$

Then

$$(11) \quad \Phi = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{rs} (Z) e^{2\pi i r X \cos \phi / \lambda^*} e^{2\pi i s \nu^* t}$$

In the case of a progressive sound wave

$$(12) \quad \Phi(X + \rho\lambda^* \sec \phi, Z, t) = \Phi(X, Z, t - \rho/v^*)$$

This condition restricts the number of terms in the above expansion (11) so that

$$(13) \quad \Phi = \sum_{-\infty}^{\infty} f_r(Z) e^{2\pi i r X \cos \phi / \lambda^*} e^{-2\pi i r v^* t}$$

Thus

$$(14) \quad \psi = \sum_{-\infty}^{\infty} f_r(Z) e^{2\pi i r X \cos \phi / \lambda^*} e^{2\pi i (\nu - r\nu^*) t}$$

If one considers the diffraction effects of ψ given by (14), it will be fairly obvious that the n th order will be inclined at an angle $\sin^{-1}(-n\lambda \cos \phi / \lambda^*)$ to the Z -axis and will have the frequency $\nu - n\nu^*$ with the relative intensity expression $|f_n(Z)|^2$.

3 The Case when the Disturbance in the Medium is Simple Harmonic.

If we suppose that the variation in the refractive index of the medium is simple harmonic along the x -axis, it can be represented as

$$\begin{aligned} \mu(x, t) - \mu_0 &= \mu \sin 2\pi(\nu^* t - x/\lambda^*) \\ (15) &= -\frac{\mu}{2i} \{e^{i(bx - \epsilon)} - e^{-i(bx - \epsilon)}\} \\ &= -\frac{\mu}{2i} \{e^{i(\delta X \cos \phi + Z \sin \phi - \epsilon)} - e^{-i(\delta X \cos \phi + Z \sin \phi - \epsilon)}\} \end{aligned}$$

where $\epsilon = 2\pi\nu^* t$ and $b = 2\pi/\lambda^*$.

We know from (6) that Φ satisfies the equation

$$\begin{aligned} \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial z^2} &= -\frac{4\pi^2}{\lambda^2} \{\mu(x, t)\}^2 \Phi \\ (16) \text{ or} \\ \frac{\partial^2 \Phi}{\partial X^2} + \frac{\partial^2 \Phi}{\partial Z^2} &= -\frac{4\pi^2}{\lambda^2} \{\mu(X, Z, t)\}^2 \Phi \end{aligned}$$

Substituting the Fourier series (13) and the expression (15) for $\mu(X, Z, t)$ in the equation (16) and neglecting the second order term with the coefficient μ^2 , we get by comparing the coefficients

$$\begin{aligned} (17) \quad \frac{d^2 f_r}{dZ^2} - \frac{4\pi^2 r^2 \cos^2 \phi}{\lambda^{*2}} f_r - A f_r &= \\ \frac{B}{2i} \{f_{r-1} e^{i\delta Z \sin \phi} - f_{r+1} e^{-i\delta Z \sin \phi}\} \end{aligned}$$

where $A = -4\pi^2 \mu_0^2 / \lambda^2$ and $B = 8\pi^2 \mu_0 \mu / \lambda^2$.

Putting $f_r(Z) = \exp(-i u \mu_0 Z) \Phi_r(Z)$, where $u = 2\pi/\lambda$, we get

$$(18) \quad \frac{d^2 \Phi_r}{dZ^2} - 2i u \mu_0 \frac{d\Phi_r}{dZ} - \frac{4\pi^2 r^2 \cos^2 \phi}{\lambda^{*2}} \Phi_r = -\frac{Bi}{2} \{\Phi_{r-1} e^{ibZ \sin \phi} - \Phi_{r+1} e^{-ibZ \sin \phi}\}$$

Putting $Z = (2\pi\mu)^{-1}\lambda\xi$ we obtain

$$(19) \quad \mu^2 \frac{d^2 \Phi_r}{d\xi^2} - 2i\mu_0\mu \frac{d\Phi_r}{d\xi} - \frac{r^2 \lambda^2 \cos^2 \phi}{\lambda^{*2}} \Phi_r = -\mu_0\mu i \{\Phi_{r-1} e^{ia\xi \sin \phi} - \Phi_{r+1} e^{-ia\xi \sin \phi}\}$$

where $a = \lambda/\mu\lambda^*$

As μ is of the order 10^{-5} and μ_0 is of the order unity we may omit the first term and consider the equation

$$(20) \quad 2 \frac{d\Phi_r}{d\xi} - (\Phi_{r-1} e^{ia\xi \sin \phi} - \Phi_{r+1} e^{-ia\xi \sin \phi}) = \frac{ir^2 \lambda^2 \cos^2 \phi}{\mu_0 \mu \lambda^{*2}} \Phi_r$$

The relative intensity of the r th order is given by $|\Phi_r(\xi)|^2$. We may now show that, in general, $|\Phi_r(\xi)|^2 \neq |\Phi_{-r}(\xi)|^2$. We will prove the same by assuming the contradictory result. Suppose

$$(21) \quad \Phi_r(\xi) = e^{i\rho_r} \Phi_{-r}(\xi)$$

Then we get

$$(22) \quad 2 \frac{d\Phi_{-r}}{d\xi} = (\Phi_{-r+1} e^{i(\rho_{r-1} - \rho_r) e^{ia\xi \sin \phi}} - \Phi_{-r-1} e^{i(\rho_{r+1} - \rho_r) e^{-ia\xi \sin \phi}}) = \left\{ -2i \frac{d\rho_r}{d\xi} + \frac{ir^2 \lambda^2 \cos^2 \phi}{\mu_0 \mu \lambda^{*2}} \right\} \Phi_{-r}$$

The actual equation for Φ_{-r} is

$$(23) \quad 2 \frac{d\Phi_{-r}}{d\xi} - (\Phi_{-r-1} e^{ia\xi \sin \phi} - \Phi_{-r+1} e^{-ia\xi \sin \phi}) = \frac{ir^2 \lambda^2 \cos^2 \phi}{\mu_0 \mu \lambda^{*2}} \Phi_{-r}$$

Comparing the equations, we obtain the result that they can never be identical unless $\phi = 0$ when $\rho_r = r\pi$. Thus in the case of oblique incidence in which $\phi \neq 0$.

$$(24) \quad \Phi_r(\xi) \neq e^{i\rho_r} \Phi_{-r}(\xi)$$

$$i.e., |\Phi_r(\xi)|^2 \neq |\Phi_{-r}(\xi)|^2$$

This means that the intensity of the r th order is not equal to the intensity of the $-r$ th order. Similar results corresponding to the above could be easily derived in the case of the standing sound waves on the same lines.

In case the coefficient of the term on the right-hand side of the equation (20) has no appreciable influence in the wave function and ϕ is small,

it can be shown that Φ_r approximates to the wave function given in Part II of this series of papers. In this case the diffraction pattern will be very nearly symmetrical.

4 Amplitude Changes on the Emerging Wave-Front of Light.

According to the notation of Part IV, the wave-function for a *general* periodic supersonic disturbance in the medium is given by

$$\psi = e^{2\pi i \nu t} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{r,s}(z) e^{2\pi i r x / \lambda^*} e^{2\pi i s \nu^* t}$$

in the case of the normal incidence of the incident light to the sound waves. Therefore the intensity is given by

$$|\psi|^2 = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A_{l,m} e^{2\pi i l x / \lambda^*} e^{2\pi i m \nu^* t}$$

where

$$A_{l,m} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{r,s} f_{r-l, s-m}^\dagger$$

† denoting the conjugate.

Thus, the intensity (or the amplitude) will be periodic in x and t on the wave-front which forms the basis of the explanation of the amplitude grating found by Bar² and Lucas.⁶ This forms also the basis of the explanation of the observability of the sound waves found by the investigators⁷ at Koln. In the case of a standing sound wave, the *average intensity with respect to time* will be given by

$$I(x, z) = \sum B_s B_s^\dagger$$

where

$$B_s = \sum_{r=-\infty}^{\infty} f_{r,s} e^{2\pi i r x / \lambda^*}$$

and r and s are both even integers or odd integers. It follows from the above that $I(x, z)$ is periodic in $\lambda^*/2$.

The intensity (or the amplitude) will be constant on the wave-front when all $A_{l,m}$ vanish except $A_{0,0}$ as will be so in the case governed by the restrictions of Part I.

5 Summary

The essential idea that the phenomenon of the diffraction of light by high frequency sound waves depends on the corrugated nature of the transmitted wave-front of light has been developed on general considerations in this paper to apply for the case of the oblique incidence of the incident light to the sound waves. It is found that the intensity distribution will not be symmetrical in general thus explaining the results of Debye and

Sears, Lucas and Biquard, Bär and Parthasarathy. The consideration of the amplitude changes of the traversing beam of light explains the results of Hiedemann, Bär and Lucas.

We are highly thankful to Prof. Dr. R. Bar of Zurich for having kindly sent us a copy of the proof of a paper by him describing experimental tests of our theory which is now in course of publication in the *Helvetica Physica Acta*

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ELECTRONIC CONFIGURATION AND BOND ENERGY.

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Introduction.

AMONG the many band spectra of diatomic molecules known at the present time, if one excludes the permanent gases, those of the oxides have been easily the earliest to be observed. Lately, however, the number of band spectra of fluorides, chlorides, sulphides and of a few oxides which were still unobserved have been recorded and analysed by various authors. Even now the number of molecules whose spectra one would like to know is not large but a beginning can be made by a systematic survey and comparison of available data, to understand empirically the relationship between the bond energies determined by the spectra and the place of the constituent atoms in the periodic system on the one hand and the electronic configuration of the completed molecule on the other. In this paper we propose to start such an attempt. We shall not treat the hydrides because they approach closely the united atom and are a class by themselves. The oxides and halides of the second group and the oxides of the fifth group have been dealt with recently from a similar point of view¹ and these results will be bodily taken over for our present purpose.

Electronic Configuration and Dissociation Products.

(a) *Oxides of the third group*—Since the halides of the alkali metals are electrovalent and the diatomic molecules formed by atoms of the second group are already dealt with, we start with the oxides of the third group. In addition to BO and AlO which have been known for some time we now know also GaO. Particular interest attaches itself to this because there exist two different theories on the connection between dissociation energy and electronic configuration, with which we shall deal presently below. The spectrum of BO has been discussed by Mulliken² from the view-point of his theory and that of AlO which is quite different from BO as far as dissociation energy is concerned, is discussed by Lessheim and Samuel³ from the view-point of their theory. The spectrum of GaO is therefore

likely to bring about a decision on this question as far as the oxides of the third group are concerned.

In gallium oxide one band system⁴ involving two $^3\Sigma$ terms is known for which the energy of excitation is 3.17 volts and the dissociation energies are 2.82 v. for the ground level X $^3\Sigma$ and 4.58 v. for the excited level B $^3\Sigma$. The energy difference of the products of dissociation is 4.93 v. (Fig. 1).

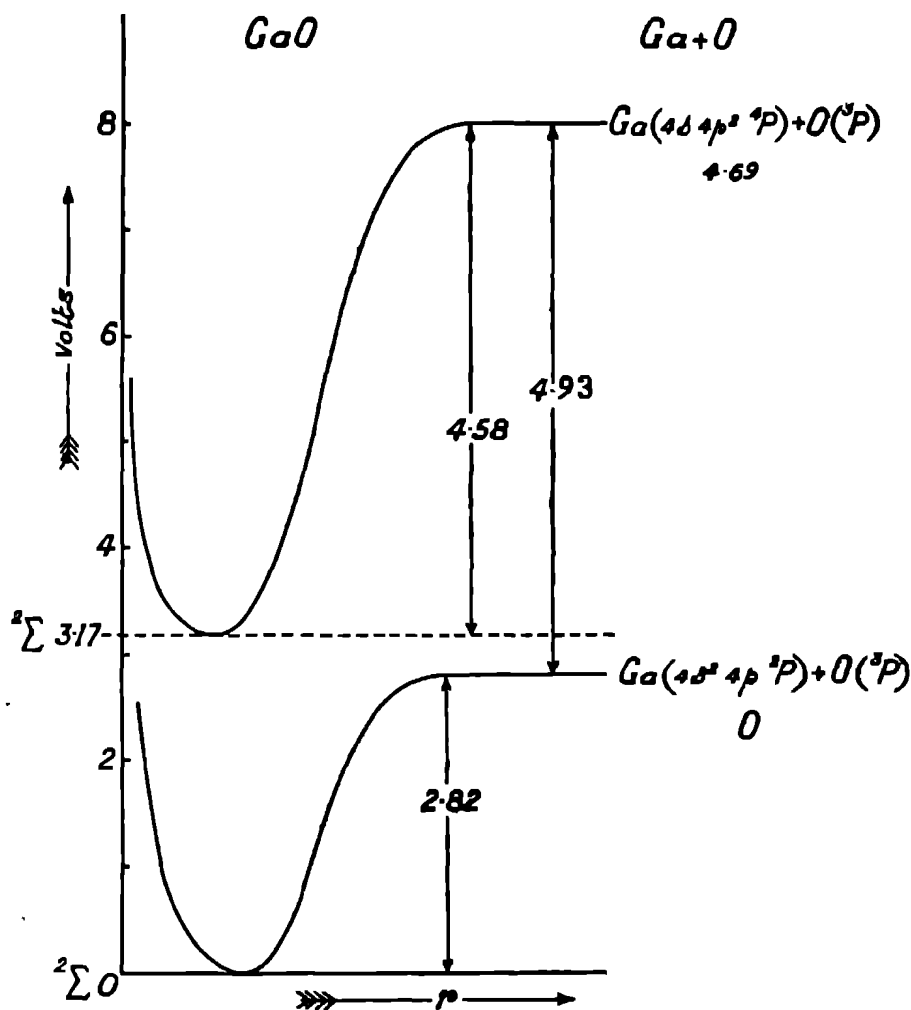


FIG. 1.

Exactly as in AlO , this constitutes a typical example of a molecule for which the dissociation energy increases on excitation.

The interpretation of such states of molecules really involves the essential difference between the two methods of treatment mentioned above. The method of molecular orbitals yields, as is well known, all the electronic configurations which give rise to the totality of electronic terms of a molecule. It is, however, not competent to distinguish the stable or attractive terms from the unstable or repulsive ones except by the introduction of

an additional hypothesis. One such hypothesis (Heizberg, Mulliken) is that the dissociation energy of a molecule is the resultant of the contributions of the single bonding and anti-bonding electrons; these are recognised as the non-promoted and promoted electron and the change of dissociation energy in the various states is attributed to the process of promotion. In the other view only those electrons contribute to the dissociation energy of a given level which, coming from different atoms, join to form pairs on the same molecular orbital. The essential difference between the two view-points therefore is that while for the first one the promotion has the first order effect and interaction between the electrons (other than that represented by a screening effect) only a subsidiary influence, exactly the reverse is true for the second method. On the basis of the latter view an increase in the dissociation energy of a molecule on excitation may then be due either to the removal of the odd electron, which represents a free valency as in BeF^\cdot or NO , or to an increase in the number of electron pairs, giving rise to an increase in the number of chemical bonds, as for instance in BeO . The oxides of the third group are further examples of the latter case. Therefore in GaO as in AlO according to this interpretation we would expect that the term with an increased energy of dissociation is formed by the combination of unexcited oxygen with the Ga atom possessing two p -electrons, the s^2 group having undergone previous fissure. This is indeed borne out by experiment. The difference in the energy of the dissociation products is 4.93 volts and represents the energy of the transition $(4s^2 4p^2 {}^2P) - (4s 4p^2 {}^4P) = 4.69$ volts, which is indeed the lowest one of all those, which possess two p -electrons. There is, however, a term in which the s^2 group is intact, *i.e.* $(4s^2 s {}^2S)$ in Ga with an excitation energy of 4.64 volts. If this term is correlated to the upper level of the band system why other similar but lower terms like $(4s^2 5s {}^2S)$ or $(4s^2 4d {}^2D)$ are passed over in the process of formation of the GaO molecule, will be completely ununderstood. On the other hand, it is particularly significant that the strongest system of the GaO bands directly gives an empirical and straightforward correlation to the configuration of Ga with two p -electrons. From the configuration $\text{Ga } (4s^2 4p^2 {}^2P) + \text{O } (2s^2 2p^4 {}^3P)$ many configurations for the molecule GaO are possible of which the following will have the lowest energy:—

$$s\sigma^2 (s), \quad p\sigma^{*2} (s), \quad p\pi^4 (p), \quad s\sigma (p) \quad {}^2\Sigma$$

According to the above correlation the excited level is obtained by a combination of Ga, $(4s 4p^2 {}^4P)$ with O, $({}^3P)$. The energetically lowest possible configuration of this combination is:—

$$s\sigma^2 (s), \quad p\sigma^* (s), \quad p\pi^4 (p), \quad s\sigma^2 (p),$$

the resulting term is indeed a ${}^2\Sigma$ in agreement with the experimental result. The increased energy of dissociation in the excited state is due to the formation of an additional bond. In the ground level, according to the conceptions of the pair-bond theory of linkage, (see below), only one bond is formed because, the s -electrons of Ga remain as a group by themselves in the GaO molecule and therefore do not take part in the linkage, and only the single p -electron joins with the electrons of O in a common molecular orbital. From a comparison of the two electronic configurations, it will be seen that the odd $s\sigma$ (p) electron belongs essentially to the O atom and that the single bond is formed in the $p\pi^4$ (p) group which is made up of three p -electrons of O and one of Ga. In the excited state this group remains intact. But the second p -electron of Ga, which is now available after the splitting of the s^2 group, joins the odd p -electron of O, completing the $s\sigma$ (p) group and thus giving rise to an additional bond.

These results are in complete harmony with those of AlO, where also the increase in dissociation energy in the excited state is brought about by an additional $p-p$ bond formed in exactly the same way. Thus among the three oxides of the third group whose spectra are known, two confirm the predictions of the pair-bond theory. The known spectra of BO alone indicate a different behaviour. The extrapolated dissociation energies correlate the lowest term of the BO molecule with excited terms of the separated atoms, and the excited terms of the normal atoms with the excited molecular state. Mulliken assumes that the extrapolated value for the lowest term of the molecule is too big and so makes it join the level of the unexcited atoms. If this is true, the term with an increased energy of dissociation, corresponding to that in GaO and AlO is not yet observed. Thus though BO does not support our explanation, it also does not contradict it. We are, however, inclined to believe that the $X\ {}^2\Sigma$ term of BO does not correspond to the ground level of GaO or AlO but to the excited level with increased energy of dissociation. From our experience about the extrapolated dissociation energy in a large number of similar molecules, we rather think that the reduction of 30% which is necessary for a correlation term of unexcited atoms is too much. The dissociation energy of this particular excited ${}^2\Sigma$ level has been found to be 4.6 volts in GaO and 6.2 volts in AlO, and therefore the extrapolated energy of 9.3 volts of $X\ {}^2\Sigma$, in BO, is about the correct order of magnitude.

(b) *Halides of the fourth group.*—Molecules possessing free valencies in the ground state are next met with among the halides of the fourth group. On account of the two p -electrons of the atoms of this group oxides and sulphides are stable molecules; the diatomic halides, however, are, from the

standpoint of chemistry, only radicals. Like molecules of the type CaF or NO , these halides of the fourth group should therefore possess excited electronic terms which are more stable than their ground levels if the electron representing the free valency is partly removed by excitation to a higher group. Among the spectra of such molecules, indeed three cases are known in which this statement has been already confirmed. These are the molecules SiF , SiCl and SnCl . Among other molecules which have been mostly observed in absorption, the corresponding term with increased energy of dissociation has not yet been found. The molecule SnCl has been already discussed earlier^{3,5} and it is shown that the combination of unexcited atoms in their configurations $\text{Sn } (5s^2 5p^2 \ ^3P)$ plus $\text{Cl } (^2P)$ gives rise to a number of terms among which the ground state $^3\Pi$ with an energy of dissociation from 3.2 to 3.5 volts is one. The electronic configuration of the molecule in this state is:—

$$\sigma^2(s), \sigma^{*2}(s), \pi^4(p), \sigma^2(p), \pi^*(p) \quad ^3\Pi.$$

By an excitation of 4.2 volts we get to a $^2\Sigma$ state of the molecule for which the energy of dissociation is 4.8 volts and which is formed by the combination of unexcited Cl and excited Sn in the configuration $(5s^2 5p 5d)$. The electronic configuration therefore is:—

$$\sigma^2(s), \sigma^{*2}(s), \pi^4(p), \sigma^2(p), \dots, \sigma(d) \quad ^2\Sigma.$$

From a comparison of the two atomic and the two molecular states it is evident that the predictions of the electron pair-bond theory are confirmed.

These conclusions are fully corroborated by two more molecules whose spectra have been recently analysed. The ground level of the molecule $\text{SiF } (^3\Pi)$, has the following configuration⁶ similar to that of SnCl :—

$$\sigma^2(s), \sigma^{*2}(s), \pi^4(p), \sigma^2(p), \pi^*(p), \quad X \ ^3\Pi.$$

It is formed by the combination of unexcited atoms $\text{Si } (3s^2 3p^2 \ ^3P) + \text{F } (^2P)$, and has an energy of dissociation of 4.77 volts. Among the excited levels there exists a term $\text{B } ^3\Sigma$ lying 4.29 volts above the ground level, having an increased energy of dissociation of 6.51 volts and the excitation energy of the products of dissociation (6.03 volts) correlates it to the level $\text{Si } (3s^2 3p 4p \ ^1S) + \text{F } (^2P)$. Its electronic configuration is:—

$$\dots \pi^4(p), \sigma^2(p), \dots, \sigma(p) \quad \text{B } ^3\Sigma.$$

It will be seen that the configuration of the molecule in which the electron which does not contribute to the linkage is removed to a higher group, possesses an increased stability. Another excited term $\text{C } ^3\Sigma$ for which the data are not very certain offers some evidence for a similar increase in stability if the non-binding electron of the Si atom is removed not to $4p$ as in the former case but to $4s$.

The data on SiCl are rather meagre and the constants are derived from but a few observations.⁷ Only one band system is known which apparently belongs to the transition ${}^2\Sigma \rightarrow {}^2\Pi$, the latter being the ground state of the molecule. The extrapolated value 4.98 volts for the ground level is much higher than what one would expect from analogy with SiF which has 4.77 volts for its dissociation energy in the ground state. Similarly there is little doubt that the extrapolated value of 11.59 volts for the energy of dissociation of the ${}^2\Sigma$ level is abnormally too high leading to an excitation energy of 10.81 volts of the dissociation products, which is too low for the first excited term of F and above the ionisation potential of Si. It is however certain that the excited ${}^2\Sigma$ level has an increased energy of dissociation and dissociates into normal F and a highly excited Si atom in which one of the *p*-electrons must have been removed to higher orbits

Dissociation Energy and Electronic Configuration.

The relation between the energy of dissociation and the electronic configuration of the molecule can be further followed throughout the periodic system. We shall compare firstly the bond energy in a class of compounds along one particular period such as, *e.g.*, the oxides of Mg, Al, Si, P, and S. This will enable us to trace the effect of the electronic configuration on the energy of the bond. Secondly, we shall follow the course of the dissociation energy along the different periods, comparing molecules such as the oxides of the fourth group, *e.g.*, CO, SiO, GeO, SnO, and PbO. This will give us the influence of the varying field strength and polarity on the energy of formation of the molecule.

In Table I we have collected the energies of dissociation in the ground state of a number of molecules. They are obtained mostly by linear extrapolation, except those of O₂ and S₂ which are obtained from the convergence limit of the absorption bands. These values do not all possess the same accuracy, the extrapolation being based in some cases on but a few vibrational levels, which are themselves obtained from only a few observations. In some cases the spectra have not been sufficiently investigated to give us the exact nature of the term and some of the data are from absorption bands alone. Especially the values in brackets appear to be much less reliable than the rest.

In the case of S₂ and CO things are not yet definite. Interpretations of rotational pre-dissociations observed in these molecules have been used to evaluate their energy of dissociation in the ground state.⁸ But these interpretations have to face some objections. Rotational pre-dissociation will certainly give rather accurate values of the heat of dissociation but it

TABLE I.*

	Be	Mg	Ca	Sr	Ba
F	5.4	3.7	3.2	3.1	
Cl	4.3	3.9	3.5		
O	5.8	3.8	3.88	3.28	
	B	Al	Ga	In	Tl
F					
Cl	3.0	3.0	(2.0)	(3.1)	(2.3)
O	(~0)	4.2	2.8		
	C	Si	Ge	Sn	Pb
F		4.8			3.4
Cl		(5.0)		3.8	3.2
O	~10	7.8	7.3	5.8	4.3
	N	P	As	Sb	Bi
F				~4	3.6
Cl					3.0
O	6.7	6.5	5.0	5.3	
	O	S	Se	Te	
O	5.00	~5.1	4.2		

* For this and the following tables the constants of the molecules are taken from W Jevons "Report on Band Spectra" (London, 1932) and H. Spöner: "Molekuel Spektren (Berlin, 1936). For PbF G D Rochester *Proc R Soc*, 1936, 153, 407, BiF, BiCl, etc F Morgan: *Phys Rev*, 1936, 49, 41. For SiF R. K. Asundi and R. Samuel (Ref 6); SbF from unpublished data

has to be established unmistakably as for instance in the case of MgH. Otherwise it will be difficult to distinguish between true rotational pre-dissociation for which a correlation to atomic levels is possible and the simple termination of band structure arising from rotational instability or from experimental conditions of excitation. In CO, for instance, the suggested interpretation is not compatible with Kronig's selection rule for multiplicity and the value of 8.41 volts for D (CO) leads to 107.9 K.cal/mol. for the heat of sublimation of carbon, a value which hardly can be reconciled with thermochemical data and particularly the behaviour of free radicals. In S₂ we have means of checking the interpretation of the abrupt termination of the rotational structure as genuine pre-dissociation. As we know,

the point of convergence in an absorption band spectrum is also one of the most accurate methods of deriving the energy of dissociation. Such a convergence limit for S_2 is found at 4.9 ± 0.2 volts.⁹ If the dissociation products are normal atoms, this value is itself equal to $D(S_2)$, or if we deduct once or twice the triplet separation of $S(^3P)$, we obtain 0.07 or 0.14 volts less. On the other hand, if the products of dissociation involve a sulphur atom in the 1D term, we obtain 3.8 ± 0.2 volts for $D(S_2)$. None of these possible values agrees with 4.41 volts which is deduced from the interpretation of disappearance of rotational structure as true pre-dissociation. The wide discrepancy between the values on this interpretation and the data on convergence limit shows that the interpretations of pre-dissociation data are not always easy. For our present purpose therefore we take the values of ~ 10 volts of $D(CO)$ and 3.8 volts for $D(S_2)$.

In spite of these difficulties certain characteristic changes do exhibit themselves quite clearly and we proceed to point out and discuss them. If we compare the diatomic *halides*, we find that the dissociation energy

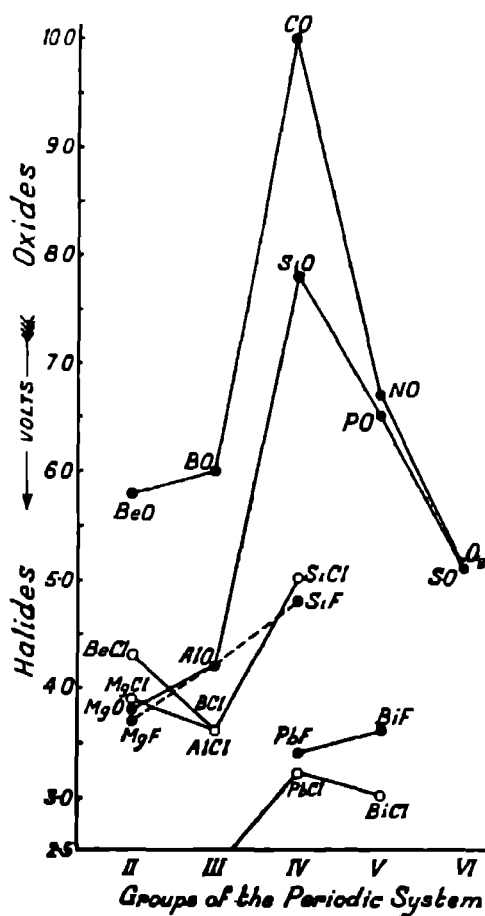


FIG. 2.

remains rather constant in the same period as will be seen also from the examples displayed in the diagram. There are slight differences, which indicate only a secondary superimposed effect. On the other hand, the energy appears to decrease from the second to the third group, but seems to rise again in the fourth group with a tendency to be rather constant later on. For example, BeCl has 4.3, BCl 3.6 volts showing the decrease from the second to the third group AlCl with 3.6 and SiCl with something less than 5 volts indicate the increase from the third to the fourth group and so also do TlCl with 2.3 and PbCl with 3.2 volts. BiCl with 3.0 indicates a tendency for the dissociation energy to remain constant from the fourth to the fifth group.

We shall consider these tendencies from the view-point of the method of molecular orbitals. Firstly let us assume according to the original interpretation of this method, that each single electron contributes independently to the stability of the molecule as a bonding electron if it is not promoted, as an anti-bonding one, if it is promoted. From this standpoint, the ground levels, of all the halides involve unexcited atoms. The outside *s*-electrons of the metal and the halogen form an unpromoted and a promoted σ^2 group, whose contributions to the bond cancel out and the linkage is produced by the *p*-electrons of the halogen atom alone in the earth alkali halides, and of the metal and the halogen both in the subsequent groups. Accordingly we get 5 unpromoted electrons in compounds like BeCl and 6 such electrons in BCl. The additional electrons in molecules of the subsequent types come now into non-promoted groups and SiF processes 6 bonding and 1 anti-bonding electron ($\pi^4 \sigma^2 \pi^*$), BiF 6 bonding and 2 anti-bonding electrons ($\pi^4 \sigma^2 \pi^{*2}$). Each electron represents half a positive or negative bond, as a consequence of which BeCl has $2\frac{1}{2}$, BCl 3, SiF $2\frac{1}{2}$ and BiF 2 bonds. This should show itself in an increase of the bond energy from BeCl to BCl, and a decrease from AlCl to SiCl, while just the reverse happens in each case. Here we have assumed, that all the *p*-electrons are on molecular orbitals. If it is presumed, that four of the *p*-electrons of the halogen remain on atomic orbitals, the disagreement is even more pronounced, because the percentage changes become bigger.

The other standpoint does not meet with any such difficulties. Here we obtain only a single bond in every case, because only such electron pairs contribute to the stability of the molecule in which electrons of both the atoms join, and because 4 of the *p*-electrons of the halogen atom form a π^4 group by themselves, only one electron joins in the same orbital with electrons of the metal atoms. The halides of the second group are formed according to this view by excited metal atoms with one *s*- and one *p*-electron,

for which experimental evidence seems to be convincing.¹ In BCl, SiF and BiF the metal atom possesses already a p -electron and is therefore capable of chemical union in its unexcited state. Thus we obtain everywhere the same type of a single p — p bond on which is superimposed the varying influence of the remaining electrons. An odd electron not contributing to the linkage may disturb and weaken it, but on the other hand, a hybridisation, *e.g.*, of the s and p functions as for instance in BeCl, may slightly strengthen the bond. Subject to such considerations this view-point certainly explains the course of the dissociation energy satisfactorily.

The superiority of this view-point becomes more evident from the following discussion of the *oxides*. In an oxide of the second group, according to the original interpretation of the method of molecular orbitals, again the two $\sigma^2(s)$ groups cancel out and the linkage rests on the four p -electron of oxygen alone, which are bonding electrons in the molecule. The ground state of the molecule being $^1\Sigma$ and that of O being 3P , this interpretation has to assume, that it involves an oxygen atom already excited to 1D . But also the combination of an unexcited metal atom of the second group with unexcited oxygen gives a bonding configuration with the same 4 unpromoted p -electrons of O and the resulting triplet term of the molecule should form either the ground level or at least a very low term in the electronic states of the molecules. But such a term has never been found. In any case oxygen having one electron less than a halogen, we obtain electronic configurations with one electron less than in the halides and accordingly 2 bonds in BeO, $2\frac{1}{2}$ in AlO, 3 in CO, $2\frac{1}{2}$ in NO, and 2 in O₂.

From the other view-point the known ground level $^1\Sigma$ of the earth alkali oxides is formed by neutral oxygen and a metal atom in the term sp 3P . This has been corroborated by the correlation of the dissociation products of the higher electronic states of these molecules to atomic terms and particularly the occurrence of the anomalous terms of the metals leaves little doubt as to the justification of this correlation.¹ The molecules of the type of BeO possess therefore only a single bond in their ground state which has to be considered as a p — p or a hybridised sp — p bond. The oxides of atoms of the third group also possess only a single bond in their ground level, because only one p -electron is present in such unexcited metal atoms. The atoms of the fourth group are the first to possess two p -electrons in their unexcited state and therefore their oxides possess a double bond. The same holds for the atoms of the fifth and sixth groups, but their oxides possess one and two odd electrons respectively, which disturb and weaken the bond in the ground state.

Experimentally we find that the energy of dissociation remains constant or rather decreases from MgO and CaO to AlO and GaO *. From the discussion about BO, above, it is clear that the dissociation energy of unexcited BO is about 6 volts, whether the observed $^3\Sigma$ level is the ground level or not. This value is again identical with that of BeO and considerably less than that of CO. If we compare the oxides of the atoms of the fourth group with the corresponding oxides of the second and third group, we get the interesting result, that the energy of dissociation shows a big increase and is about doubled. In the next groups, molecules of the NO and SO types, the dissociation energy is again decreased in two distinct steps.

The decrease of energy as we go from the fourth group to the sixth finds its explanation equally well from both the above view-points, from the assumption of promotion in the one case, and from that of the disturbing effect of the odd electrons in the other. On the other hand, the observed change from the second group to the third and fourth groups, can only be explained by the second view-point. From the first view-point a regular increase would be expected, so that the oxide of the atoms of the third group would have a dissociation energy midway between the oxides of those of the second and fourth. But, as the discussion in the first section of this paper has shown, BO, AlO, and GaO possess about the same dissociation energy as the corresponding oxides BeO, MgO and CaO, and one half to two thirds of that of CO, SiO, and GeO. From the second view-point such a course of the dissociation energy is just what one would expect. So long as a single bond persists as it does in the oxides of the second and the third groups, the dissociation energy is roughly of the same order of magnitude; as soon, however, as we reach the fourth group where the pure double bond manifests itself without the presence of disturbing electrons, the dissociation energy suddenly increases to nearly double the value. This to our mind indicates another evidence in favour of an interpretation of the method of molecular orbitals as an electron pair-bond theory of valency.

We shall now follow the course of the dissociation energy along different periods, comparing for instance the oxides and sulphides of the fourth group with each other, the spectra of these molecules being known better than of those in any other period. It can be seen from Table II that the energy of dissociation decreases as we proceed along a row or go down along a column. This means that the bond energy runs parallel to the field strength, with no regard to the polarity of the molecule. From CO to PbO

* The departure of GaO from CaO is much more pronounced than that of AlO from MgO, but we believe that the value of CaO is slightly too high because it cannot be higher than that of MgO.

TABLE II.

	C	Si	Ge	Sn	Pb
O	~10	7.8	7.3	5.8	4.3
S	7.8		5.7	5.5	4.7
Se	4.2				

the bond energy decreases, whereas the polarity increases, while from CO to CSe both decrease together. It has been pointed out already elsewhere¹⁰ that such a course is not compatible with a theory in which each single electron contributes independently towards the energy of formation. In such a theory the wavemechanical interaction of the electrons (other than that represented by a simple screening effect), is neglected and the bonding effect is due to the degeneracy of the nuclear fields. But the polarity is another expression for the dissymmetry of the nuclear fields and this theory should predict the bond energy and the polarity to run together. That is another instance again in favour of the electron pair-bond theory of valency.

The difference between the two interpretations of the method of molecular orbitals shows itself in polyatomic molecules as the difference of non-localised and localised bonds. With the exception probably of hydrides and certainly of aromatic compounds, where non-localised electrons are present, brought about by hybridisation of the localised bonds, and where they just produce the specific aromatic character, the pair-bond theory of valency leads to localised bonds as a result of the wavemechanical interaction, mentioned above, while its neglect leads to non-localised bonds, and this neglect is necessary if the energy of formation of a molecule shall be conceived as the sum of the contributions of individual independent electrons. We have shown elsewhere,¹¹ that a close correspondence exists among the ω values known from infra-red and Raman spectra of certain polyatomic molecules and those of the constituent diatomic radicals, known from band spectra. Though the number of such instances known is not very large at the present moment, we believe that the coincidences are not fortuitous and that they therefore favour the conception of localised bonds. We have further tried to follow this correspondence in respect of dissociation energies. In the case of the chlorides and oxychlorides of di- and tetravalent sulphur a correlation between the bond energies could be established by their photodissociation¹² and it was found, that, *e.g.*, the S = S bond has the same energy in polyatomic molecules as is obtained from the band spectrum of S₂. An

extension of such a correlation to other molecules is not so conclusively possible for want of sufficient and reliable data. In spite of this we should like to point out certain interesting features among the available instances. The values of dissociation energy obtained from the usual linear extrapolation of vibrational levels are by no means satisfactory in many cases, if taken individually. But there seems to be little doubt that the errors thus introduced cancel out, probably because they are in the same direction, when we correlate the products of dissociation in different electronic states of one and the same molecule to the terms of the constituent atoms. For our present purpose we shall have to use individual values which therefore are not absolutely correct and therefore are expected to differ from the thermochemical values

Among the few instances, which are available for such a comparison there are some, which exhibit a close relation between the bond energies of the diatomic radical molecule and the saturated chemical molecule. Denoting by D_0 values from the dissociation energy derived from band spectra and by D_r such from thermochemical measurements (both in volts), we collect them in the following table :—

TABLE III.

	D_0	D_r	D_r'
AgO	1.8	$1/2 D_r (\text{Ag}_2\text{O}) = 1.9$	
PbCl	3.3	$1/2 D_r (\text{PbCl}_2) = 3.4$	$1/4 D_r (\text{PbCl}_4) = 2.1$
BiCl	3.6	$1/3 D_r (\text{BiCl}_3) = 3.3$	
BiBr	2.7	$1/3 D_r (\text{BiBr}_3) = 2.4$	
SbF*	~4	$1/3 D_r (\text{SbF}_3) = 4.6 (5.6)$	
SO	5.1	$1/2 D_r (\text{SO}_2) = 5.4$	$1/3 D_r (\text{SO}_3) = 4.7$
SeO	4.2	$1/2 D_r (\text{SeO}_2) = 4.5$	$1/3 D_r (\text{SeO}_3) = 3.7$

* For the thermochemical energy of formation two values exist in literature, which lead to 4.6 and 5.6 volts, respectively (*cf.* Mellor).

It is interesting to note, that where a comparison is possible, D_0 agrees better with the thermochemical value derived from the molecule with lower valency than from that with maximal valency of the central atom. The best known example for such a behaviour is of course CO, where $D_r (\text{CO})$

gives 235 K.cal./mol., $\frac{1}{2} D(\text{CO}_2)$ 181 K.cal./mol. This is connected with the fact, that the D_r values for such molecules with maximal valency are not bond energies at all, *i.e.*, do not refer to the *adiabatic* dissociation by excitation of the vibrational levels, because the ground level of a molecule like CO_2 or SO_2 is not formed by the combination of unexcited CO or SO_2 and unexcited O atom. This is clear from the diamagnetic character of these molecules and absorption spectra indicate, that the halides of the maximal and minor state of values are in a similar relation¹² at least from the fourth group of the periodic system onwards. It cannot be said for certain whether the ground level of a molecule like SO_2 involves excited oxygen atoms or excited SO_2 molecules, but since the pair-bond view would be better satisfied by the splitting off of the original s^2 group of S, the above relation appears again to favour the latter standpoint.

It is further interesting to note, that in cases like AsO and SbO the values $\frac{1}{2} D_r(\text{As}_2\text{O}_3) = 7.6$ and $\frac{1}{2} D_r(\text{Sb}_2\text{O}_3) = 7.3$ volts agree better with the dissociation energy of those terms of AsO and SbO in which the odd electron is already partly removed. The dissociation energy of the ground level of AsO is 5.0, that of the $B^2\Sigma$ term is 6.1; the corresponding figures for SbO are 5.3 and 6.2 volts. The energies of formation of N_2O_3 and P_2O_3 are not certain, but we may expect the same relation there also.

Conclusions.

The original interpretation of the method of molecular orbitals as a theory of valency, in which the single electron possesses bonding power was based on the assumption that non-promoted electrons are bonding and promoted ones are anti-bonding or non-bonding. This assumption is not the outcome of any requirements of theory but is an empirical postulate, which seeks justification in experimental facts. Earlier attempts at correlation between the electronic levels of molecules and the energy states of the constituent atoms indeed appeared to lend support to this assumption. Later investigations have, however, shown that completely different correlations are possible and are absolutely necessary to satisfy the experimental facts. For example, in a molecule like BeO the stable triplet term, which should arise from unexcited atoms according to the older correlation, is not found and by the correlation of certain excited terms to anomalous terms of the metal atom it is shown, that a non-promoted odd electron in the configuration of the ground level lowers its dissociation energy. Similar remarks apply to the types BeF and NO and the new correlation of molecular terms to atomic states from the pair-bond view is shown to be satisfactory without exception in a larger number of molecules of these three classes, recently.

These three types represent molecules with free valencies and indeed just in such molecules the difference of the two view-points must become apparent. For other such molecules with free valencies, whose band spectrum is investigated in detail, *i.e.*, for the oxides of the third and the halides of the fourth group of the periodic system, only one example of each, *i.e.*, AlO and SnCl, was originally available. We have now shown in the present paper, that the correlation according to the pair-bond theory of valency holds also for other molecules of this type and appears to be generally valid. *All this evidence, concerning the band spectra of oxides and halides of the second, third, fourth, and fifth groups of the periodic system is definitely against the postulate of the identification of promoted and non-promoted with non-bonding and bonding electrons.* On the other hand, such a satisfactory correlation from the pair-bond view necessitates a revision of the theory of valency, based on the results of band spectroscopy.

From the purely experimental point of view an interpretation of the method of molecular orbitals as electron pair-bond theory of valency is furthermore supported by the course of the bond energies in the periodic system. The near relationship shown at the present moment in a few instances, between the bond energies of diatomic radical molecules with those of polyatomic chemical molecules, in which however the maximal valency does not manifest itself, also points in this direction. The close correspondence between the ω values of polyatomic molecules and of their radicals in the ground state in many cases and in the excited states also of some polyatomic molecules whose spectra have been recently investigated,¹¹ indicate a localisation of bonds which is the direct outcome of the pair-bond theory of valency. Further evidence in favour of this view is afforded by absorption spectra and photo-dissociation of halides and oxyhalides of di- and tetravalent sulphur, selenium, and tellurium, all of which show almost a rigorous constancy of each bond energy. To our mind, therefore, all this spectroscopical evidence undoubtedly bears out the electron pair-bond theory of valency.

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ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

Part III. Esters and Ethers.

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1. Introduction.

IN Part I¹ of the series, the ultrasonic velocities in several organic liquids were given and their relationship to chemical constitution was pointed out. In Part II² the velocities in several di-esters were determined, and the effect of lengthening of the chain, of methyl and ethyl radicals and several other features not reported earlier were discussed. The present paper forms a continuation of the series, the investigation being mainly confined to esters (mono-) and ethers.

The determination of the ultrasonic velocity was made by the diffraction of light by high frequency sound waves and the experimental details of arrangement and set-up were given in the first paper. The arrangement was the same as before.

Pure liquids were used after distillation.

The frequency of vibration employed was 7.382×10^6 c/s, but it was also checked every now and then, being corrected if there was any change.

The temperature noted against each liquid is that of the liquid itself, measured just at the time of taking the diffraction spectra.

2 Results.

Table I (given on page 483) gives ultrasonic velocities in some ethers and esters, and also adiabatic compressibilities calculated from such velocities.

No determination of velocity of sound seems to have been made for any of these compounds.

Even data of adiabatic compressibilities are few and below (Table II) is given a comparative table for such of those as are known so far. They are taken from a paper by H. Shiba.³

TABLE I. Ultrasonic velocities in organic liquids at 7.382×10^6 c/s.

	Liquids	Chemical Formula	Temp in °C.	Velocity of sound in meters/second	Adiabatic compressibility $\beta\phi \times 10^6$
	A. ETHERS:				
1	Resorcin monomethyl ether	$C_6H_4(OH)(OCH_3)$	26.0	1629	32.9
2	Resorcin dimethyl ether	$C_6H_4(OCH_3)_2$	26.0	1460	44.5
3	O-cresol methyl ether	$C_6H_4(CH_3)(OCH_3)$	26.5	1385	53.0
4	m-cresol methyl ether	$C_6H_4(CH_3)(OCH_3)$	26.0	1385	53.4
5	O-cresol ethyl ether	$C_6H_4(CH_3)(OC_2H_5)$	25.0	1315	61.2
6	Anisol	$C_6H_5 \cdot O \cdot CH_3$	26.0	1453	48.0
7	Phenetole	$C_6H_5 \cdot O \cdot C_2H_5$	25.5	1361	56.1
8	Amyl ether (iso)	$C_5H_{11} \cdot O \cdot C_5H_{11}$	26.0	1153	97.2
	B. ESTERS.				
9	Propyl acetate (<i>n</i>)	$CH_3 \cdot COOC_3H_7$	26.0	1182	80.3
10	Butyl acetate (<i>n</i>)	$CH_3 \cdot COOC_4H_9$	26.0	1179	82.6
11	Amyl acetate (iso)	$CH_3 \cdot COO \cdot C_5H_{11}$	26.0	1168	83.8
12	Amyl formate	$H \cdot COO \cdot C_5H_{11}$	26.0	1201	79.8
13	Methyl chloracetate	$CH_2Cl \cdot COOCH_3$	26.0	1331	45.8
14	Ethyl monochloracetate	$CH_2Cl \cdot COOC_2H_5$	25.5	1234	56.6
15	Ethyl acetoacetate	$CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$	25.5	1417	48.8
16	α -Picoline*	$C_6H_4N \cdot CH_3$	28	1453	49.9

TABLE II. Comparison of values for adiabatic compressibilities

Liquids	Shiba		Author	
	$\beta\phi \times 10^6$	T°	$\beta\phi \times 10^6$	T°
Propyl acetate (<i>n</i>)	85.2	25°	80.3	26
Butyl acetate (<i>n</i>)	82.6	25°	82.6	26
Amyl acetate (iso)	82.4	25°	83.8	26

* By an oversight the velocity of sound in α -picoline was given in Part I, exactly 2/3 the value it should have; the corrected value is 1491 m/s at 24°. The velocity given here is at 28°C. and the agreement is good, if allowance is made for the temperature coefficient of velocity.

Except for propyl acetate, for which Shiba's value is a little high, the agreement in the two sets of values for $\beta\phi$ is good.

3. Discussion.

Determination of ultrasonic velocities in related compounds of ethers and esters makes it possible to discuss the relationship between sound velocities and chemical constitution. The ground was covered in a general way in Part I. We shall examine the ethers and esters more closely in this paper, from the results given here.

A. Ethers.

Resorcin ethers.—The monomethyl ether shows higher sound velocity than the dimethyl ether. This is mostly due to the influence of (OH) group in the monomethyl ether, which gives it greater electric moment.

Cresol methyl ethers—In the toluidines and the xylenes, the sound velocity in the ortho-compound was found to be appreciably higher than that for the meta- or the para-compound. In the two ethers, cresol methyl ethers, however no such difference could be noticed.

Methyl and ethyl ethers—Data are available here to compare the two ortho-ethers, (a) O-cresol methyl ether and (b) O-cresol ethyl ether. The methyl ether has a decidedly higher velocity, even allowing for the small difference in their temperatures at which they were investigated. Such an increase in the velocity for a methyl compound was noticed for esters, the methyl ester showing always higher velocity than the ethyl ester of the same acid. Here we have an analogous case, for the methoxy radical behaves in a similar way. In both the types of compounds two carbon atoms are linked through an oxygen atom.

Anisol and phenetole—Anisol is the phenyl methyl ether, while the corresponding ethyl ether is phenetole. The same argument of the methoxy group giving greater sound velocity applies also here. The behaviour of esters and ethers is different from other compounds in this respect, that though ethyl radical increases the chain in length, gives, in fact, less sound velocity than the methyl compound.

Aliphatic and aromatic ethers.—The sound velocity for anyl ether has been redetermined under the same conditions, and gives, if allowance is made for the temperature correction, good agreement with the value previously determined. A review of all the data on aliphatic and aromatic ethers makes one surmise that the sound velocities in the aromatic series are, in general, higher. Such a view was also expressed with regard to the hydrocarbons, and other substituted compounds. It is extended to the class of ethers.

B. Esters.

Acetates.—The three acetates, propyl, butyl and amyl acetates have been experimented on for sound velocity at the same temperature, namely 26° C. As before, we find that with increase in the length of the alcohol radical, the sound velocity decreases markedly, at least the difference between the first and the last member is noticeable. This follows from the general conditions in Parts I and II.

Amyl esters.—It has been observed before, that even by lengthening the acid radical, instead of the alcohol, lowers appreciably the sound velocity for even two successive members of any series. As examples we took before, the ethyl esters of formic, acetic, propionic and butyric acids and showed that the sound velocity decreased from member to member, in spite of the increase in the length of the chain. Even so, here, amyl formate has higher sound velocity than amyl acetate.

Chloracetates.—The sound velocity in methyl chloracetate is 1331 meters/second at 26° C. and that in ethyl chloracetate is only 1234 meters/second at 25°·5 C. This is not surprising in view of what has been repeatedly said, on the effect of substitution of a methyl radical in place of ethyl, in esters.

Acetates and Chloracetates.—It was remarked in Paper I that substitution of a heavy atom generally lowered the sound velocity, as for example in the series, methylene chloride, chloroform and carbon-tetrachloride. However, we find that a similar substitution of a heavy atom in the esters, results in enhancing the velocity. This is borne out in the following Table

TABLE III.

Ester	Sound velocity in m/s	T °C.
Methyl acetate	1211	24
Methyl chloracetate	1331	26
Ethyl acetate	1187	23·5
Ethyl chloracetate	1234	25·5

Ethyl acetoacetate.—The sound velocity in this compound is rather high for a mono-ester, especially for a long chain molecule like this one. However, since there is a ketonic group, and as we have noticed already in

ketones, as in other classes than ethers and esters, lengthening of the chain indicates higher sound velocity, we can attribute this higher velocity to the presence of the ketonic group.

The author's best thanks are due to Sir C. V. Raman for his interest in the work.

Summary.

Ultrasonic velocities have been determined for a number of ethers and esters. They are correlated to chemical constitution and in general we may conclude (a) *that for ethers* (1) methyl and methoxy groups seem to favour greater sound velocity compared to ethyl and ethoxy groups, and (2) aromatic ethers show higher velocities than those of the aliphatic series; and (b) *that for esters* (1) heavier acid or alcohol radical lowers sound velocity in spite of lengthening of the chain, and (2) the introduction of a heavy atom like chlorine in the acid radical enhances the velocity, as against diminution in velocity observed in the series methylene chloride, chloroform and carbon-tetrachloride. Some points of similarity between ethers and esters, with regard to the sound velocity, are pointed out.

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ON THE ABSORPTION SPECTRA AND LINKAGE OF INORGANIC NITRATES AND SULPHATES IN THE VAPOUR STATE.

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*Introduction.*¹

EXPERIMENTS of Franck and his collaborators² have shown that absorption spectra of diatomic salts in the vapour state are well qualified to distinguish between covalent and electrovalent linkage in such molecules.* Whereas alkali halides are electrovalent in the vapour state, as one would expect, halides of the first sub-group of the periodic table, like those of silver, were found to possess a covalent bond and furnished for the first time a clear example, that a particular bond may change its character and be either covalent or electrovalent in the same molecule according to the experimental conditions. This result, at the first moment surprising, is naturally of great interest for any physical understanding of chemical linkage and made it desirable to extend such investigations to polyatomic molecules.

The criterion by which Franck was able to distinguish between atomic and ionic binding, was that the term of a molecule which originates in two neutral and unexcited atoms, naturally is the ground level of a covalent molecule but forms an excited term of an electrovalent one, because here the ground level is formed by a combination of two ions. This criterion cannot be used in the case of polyatomic molecules. Firstly, it is known on

* A bond is termed 'covalent' here if the molecule dissociates into neutral atoms by adiabatic excitation of the vibrational levels of its ground state, and 'electrovalent' if this adiabatic dissociation produces ions. We thus identify the chemical terminology with that of Franck (atomic molecules and ionic molecules), but it should be clearly understood, that we speak of the character of the bond of a molecule only under well-defined experimental condition. It will be seen, that a bond, *e.g.*, that between potassium and oxygen in KNO_3 , may be covalent in the vapour state and electrovalent in solution on account of the additional energy of hydration. Only with this proviso it is permissible to identify the chemical terminology with the above definition without confusion. A covalent bond may be polarised or not and the molecule possessing a dipole moment or not will be termed a polar, a non-polar molecule respectively, according to the terminology, introduced by Debye.

account of later investigations, that this criterion is not rigorously valid, partly because the combination of two atoms in particular states may give rise to a large number of attractive and repulsive terms, and partly because inter-sections of the potential curves of the electronic terms among themselves are quite possible. The chlorides and oxychlorides formed by atoms of the sixth group are examples of the first type.³ According to their absorption spectra they dissociate in their region of selective absorption with lowest energy into normal atoms, but chemical and physico-chemical evidence (like conductivity, Raman effect, etc) show, that they still possess a covalent bond in the liquid state and in solutions and we have to conclude *a fortiori* that they will possess a covalent bond in the vapour state, because even the additional energies of hydration or association, produced by the dipole moments of the surrounding molecules, have not been strong enough to turn the covalent bond into an electrovalent one. In some cases the Raman effect is observed directly in the gaseous state and according to Placzek's theory,⁴ the Raman effect, depending on the change of polarisation with the internuclear distance, is a criterion of covalent linkage. The results of absorption spectroscopy of polyatomic molecules are, however, not surprising, since the number of repulsive terms increases rapidly with the number of constituent atoms and the excitation of an electron by illumination apparently means the transition from the ground level of the molecule to an excited repulsive term, both together possessing the same level of unexcited atoms as that of the dissociation products. This is equivalent to an intersection of the two potential curves at large internuclear distance and may be taken as a special case of the second possibility, mentioned above. The dissociation of the ground level of a covalent molecule into excited atoms and that of an excited molecular term into unexcited atoms owing to the intersection of two curves of the Franck-Condon diagram at small internuclear distance appear to be realised in a case like CaO. Photodissociation into unexcited atoms obtains according to the continuous absorption spectrum,⁵ whereas the band spectrum indicates a covalent molecule in the vapour state and no perturbations have been found, warranting an explanation on the assumption of an hybridisation of the ionic and the atomic potential curve. It has been shown⁶ that the ground level of such molecules does not arise from that of the two unexcited atoms but involves an excited metal atom in the state sp^3P . The metal atom in its normal state 1S , the electrons forming a closed group, s^2 , gives rise to a repulsive curve which intersects that of the ground state of the molecule. Apparently this repulsive level which involves unexcited atoms forms the final state of the photolytic process. Experimentally the repulsive character of the

s^2 configuration has been definitely confirmed by the band spectrum of CdF, where the discrepancy between the energies of excitation of the dissociation products and the energy differences between the excited terms and the ground state of Cd is too large to be explained by an inaccuracy of the Birge-Sponer method of linear extrapolation⁷

Besides these theoretical considerations also practical reasons do not permit the application of Franck's criterion to polyatomic salts. The fact, that the first photodissociation produces unexcited atoms in the alkali salts, was established by the agreement of the energy difference of the various regions of selective absorption with those of the atoms concerned. This procedure is not possible for polyatomic salts, because the electronic levels of the ions or radicals such as NO_3^- or the $-\text{O}-\text{NO}_2$ group are not known. We have therefore taken absorption spectra of some polyatomic inorganic salts where it is possible to distinguish empirically between the spectrum of the covalent and the electrovalent form. Thus the spectrum of inorganic nitrates in solution is known along with that of HNO_3 and ethyl nitrate in the vapour state, that of potassium sulphate in solution along with dimethyl sulphate and diethyl sulphate in substance and in solution of ether and that of the nitrite ion is known as well as that of ethyl nitrite in the vapour state. In all these cases the absorption spectrum of the covalent form, *e.g.*, of the organic ester differs from that of the free ion in dilute aqueous solution and allows us to distinguish the electrovalent form from it. Details will be discussed below. Such compounds like nitrates appear to be suitable also because their decomposition on heating invariably liberates rather large quantities of NO_2 , which can be recognised easily by its two characteristic sets of bands the first being at about 6000 to 3500 A.U., and the second one from about 2400 A.U., onwards. It can be assumed, that the measured absorption spectra really correspond to that of the non-decomposed substance as long as these bands do not appear on the plates. The same bands served as an indicator of decomposition for potassium nitrite and those of SO_3 at about 3000 A.U., and 2200 A.U., in the case of the sulphates. It will be seen that among the nitrates those of the alkali metals stand heating better than silver nitrate, and among the divalent nitrates $\text{Cd}(\text{NO}_3)_2$ decomposes very rapidly, $\text{Pb}(\text{NO}_3)_2$ and still more $\text{Mg}(\text{NO}_3)_2$ can be heated to higher temperatures. Again Ag_2SO_4 decomposes much more rapidly than K_2SO_4 and our impression according to these few experiments is, that decomposition on heating obtains the earlier, the higher the ionisation potential of the metal atom or, what is the same, the more the molecule becomes non-polar and the more it approaches the true homopolar type of binding. On the other hand, the stability of

more complex molecules is naturally decreased very much and ammonium salts decompose at comparatively low temperatures. It was possible to study the absorption spectrum of ammonium nitrate but the decomposition of ammonium sulphate was so rapid and the amount of SO_2 liberated at low temperatures so great, that its spectrum could not be investigated

Absorption Spectra of Related Substances and of Salts in Solution

The absorption spectrum of the nitrate ion has been investigated by a number of authors and is very well known indeed, so much so that it is sometimes recommended for calibration purposes.⁸ According to qualitative measurements of Hartley and K. Schæfer⁹ the spectrum of nitric acid in diluted solutions in concentrations from 0.2 *m* to about 10 *m* exhibits a maximum in the region of 300 *mμ*. Such a maximum is also characteristic for the nitrates of the alkali and earth alkali metals in solution. The maximum disappears gradually, with higher concentrations of the acid, up to 23.12 *m* (98.6% acid), it flattens out more and more, until a continuous end-absorption remains with a point of inflection in the region between 263 and about 273 *mμ*. Schæfer and Hantzsch¹⁰ ascribed the maximum of selective absorption at 300 *mμ* in very diluted aqueous solutions to the nitrate ion, the end-absorption with the superimposed flat maximum at about 265 *mμ* of the highly concentrated solutions to a covalent molecule H-O-NO_2 .

Quantitative measurements of the absorption curve of nitrates and nitric acid in various solvents by v. Halban¹¹ and Scheribe¹² have confirmed this point of view. Mention may be made of the spectrum of nitric acid in hexane and of ethyl nitrate in the liquid state and in solution which show again a diffuse maximum at about 272 *mμ* where as the distinct maximum of inorganic nitrates in solutions of low concentrations lies at 302 *mμ*. Finally the absorption curve of ethyl nitrate in the vapour state was measured quantitatively by J. W. Goodeve,¹³ who obtained again a point of inflection between 278 *mμ* and 244 *mμ*. There is no doubt that these measurements establish a spectroscopical criterion which enables us to distinguish between the true electrovalent and the true covalent bond in this particular case. The former one, *i.e.*, the free nitrate ion exhibits a maximum of selective absorption at 302 *mμ*, but whenever the linkage between the NO_3 group and the positive partner of the molecule is due to atomic binding and not to electrostatic forces between ions, this maximum disappears and is replaced by a very diffuse one, whose highest point is difficult to measure and sometimes not at all, but which lies approximately between 263 and 275 *mμ*.

This interpretation of the spectrum in solutions of very low and very high concentrations is generally accepted, but that of solutions of nitrates

and nitric acid of medium strength, up to about 10 *m*, is more difficult. The spectrum of diluted solution of nitric acid and that of inorganic nitrates in highly concentrated solutions and in the presence of foreign ions still show a distinct maximum in the region of 300 *mμ*, but its wave-length and intensity varies from that of the undisturbed nitrate ion. Similar phenomena obtain for aqueous solutions of the acid of medium concentrations and for diluted solutions of HNO₃ in other acids like HClO₄ a.o. Also KNO₃ in highly concentrated solutions of H₂SO₄ (80 to 95% in the presence of SO₃) shows the characteristic curve of the acid. Sometimes, particularly in solution in ether, the point of inflection (what we called the diffuse maximum) due to the covalent H-O-NO₂ molecule develops to a slightly more distinct maximum at 265 *mμ* and the same is true for solution in highly concentrated HClO₄.

Hantzsch and Schæfer tried to account for all these phenomena by various equilibria between the electrovalent form $\text{O}_2\text{NO}^- + \text{H}^+$ and the covalent form O_2NOH . They assumed a high percentage of covalent molecules not only in strongly concentrated aqueous solutions of nitric acid (*c* = 10 *m* and more) but also in solutions of medium strength (between 1 and 10 *m*). Halban and his collaborators contradicted this interpretation for concentrations of medium strength on account of their new measurements carried out under various conditions. They showed, that a high percentage of covalent molecules in solutions up to 10 *m* does not agree with other physico-chemical measurements (such as conductivity, partial pressure, etc.) and assumed for the explanation of the various observed optical effects a third form of nitric acid between the covalent and the electrovalent one.

Solutions of strong electrolytes at high concentrations, *i.e.*, in that region in which the theory of Debye-Hueckel does not hold any longer, possess a more complicated structure than was originally assumed. Much of the above controversy was doubtless due to the fact, that some years ago the knowledge of the condition prevailing in such highly concentrated solutions was even less than what it is to-day. Recent investigations of Scheibe¹² and von Halban and his collaborators¹¹ themselves on the absorption spectra of organic and inorganic molecules under various conditions and some work on complex salts carried out in this laboratory on similar lines¹⁴ have shown that quite different effects obtain, qualified to change the absorption spectrum quite considerably in highly concentrated solutions or in the presence of foreign ions. We have at least to distinguish the effects of dehydration, of deformation and of a change of the probability of transition (of the amplitude of the classical dispersion formula) alone resulting from various degrees and kinds of polarisation owing to the interaction of the absorbing ion with other ions or the dipole molecules of the solvent. The probable

change of the absorption curve of cations and anions on account of these effects has been tentatively discussed by several authors,¹⁴ and, for the present purpose it is sufficient to say, that these effects may produce a considerable change of the potential curves of the electronic terms and hence of the absorption spectrum. All these effects are finally due to various kinds of polarisation of the absorbing molecule and we have to conclude that the absorption spectrum of a particular molecule is not a fixed and determined quantity but depends on the state of polarisation. If this is true, some of the arguments of von Halban and collaborators do not appear to be so strong as was originally believed. If the varying polarisation of a molecule has to be considered, it is not essential, whether the absorption curve shows a point of inflection only or a slight genuine maximum at about the same wave-length. What is essential is, that the curve is not monotonous; but whether or not a diffuse or distinct maximum is developed depends on the probabilities of transition and hence on polarisability and polarisation. It is not essential, whether a maximum has been found at exactly the same wave-length under various conditions or not, since this depends on the relative position of the two potential curves concerned, which itself depends on the polarisation. Also the construction of the absorption curve of a mixture of two absorbing kinds of molecules from those of their pure solutions cannot give accurate results nor can we expect all the curves of two kinds of absorbing molecules being in equilibrium, to intersect accurately at the same wave-length,¹⁵ because Beer's law is not rigorously true, whenever the absorption depends on the polarisation as a further parameter, and therefore, *e.g.*, on the concentration.

On the other hand it is quite evident that the change observed in solutions of nitric acid of a concentration up to about 10 *m* cannot be even approximately explained by assuming high percentage of covalent molecules H-O-NO_2 . Furthermore, Hantzsch explains certain deviations by formulating the electrovalent form in solution as $[\text{NO}_3]^- [\text{H}_3\text{O}]^+$ and similarly assumes the presence of isomeric forms of the type $[\text{ON}(\text{OH})_2]^+ + [\text{NO}_3]^-$ or $[\text{ON}(\text{OH})_2]^+ + [\text{ClO}_4]^-$ in homogeneous nitric acid (in the absence of water) and in mixtures with other acids respectively. It is quite true that the hydrogen ion forms particularly stable products in association with water or any other dipole molecule, because the proton having no dimensions in the ordinary sense is able to approach closer to the centre of negative polarity and its distance from the nucleus of the oxygen atom may even be smaller than that of its own outside electrons, and such association products may even be present in mixed crystals or solid solutions, but it remains doubtful whether such formulations serve a useful purpose. They conceive such

associations as a new class of molecular formations as distinct from other products of association or hydration, whereas in reality the physical nature of the binding force is the same in the former and in the latter ones and there is only a difference of degrees not of quality between them.

Some of the differences of opinion on the structure of such solutions are, however, due simply to different points of view and therefore of terminology. Most physicists, for instance, will consider the transition from covalent to electrovalent linkage as an effect of first order; the greatest interest is then attached to the fact that the two limiting cases of very highly diluted and very highly concentrated solutions can be distinguished by the absorption curves of the nitrate ion and the covalent molecule H-O-NO_2 . The various optical effects in concentrations of medium strength are superimposed effects of second order owing to the various kinds and degrees of polarisation. The absorption curve of any concentration is considered to be due to an equilibrium of these two forms alone. For the effects in solutions of medium strength not the presence of a high percentage of the covalent form is responsible but the polarisation of the chromophoric group. Nevertheless this formulation is closer to the original theory of Hantzsch and Schaefer. The physical-chemist, on the other hand, is more inclined to treat the ionic form $\text{II}^+ + \text{NO}_3^-$ and the covalent one H-O-NO_2 as two entirely different molecules, each possessing its own characteristic absorption and consequently considers the deviation from the Debye-Hueckel theory or from Beer's law as a first order effect. Therefore he does not speak of the polarised anion but stresses more the causes of this polarisation by introducing a third electrovalent but associated form instead.

It is evident that both opinions differently expressed mean essentially the same and we have made these few remarks on the structure of nitric acid in solutions only in order to show, that these differences found in literature neither invalidate the empirical criterion for the covalent and the electrovalent linkage of the NO_3 group, (which is safely established by the two limiting cases without regard to concentrations of the acid of medium strength) nor the theory of the transition from covalent to electrovalent linkage with which we have to deal below.

This interpretation, and therefore also the spectroscopical criterion of the covalent and electrovalent bond of nitrates, is corroborated by measurements of the Raman effect,¹⁶ showing that the electrovalent form is practically alone present in aqueous solutions up to 30% and that with higher concentrations the Raman lines of the covalent form appear and gain more and more in intensity.

It is interesting to note, that the transition from covalent to electrovalent linkage depends to a very high degree on the nature of the solvent. For aqueous solutions the absorption curve of nitric acid shows an abundance of the electrovalent form up to a concentration of 9.22 *m* whereas in a concentration of 14.8 *m* a high percentage of covalent molecules is indicated. If an acid is used as solvent even in a diluted solution a great number of covalent molecules may be present, if the concentration of the acid, used as solvent, is strong enough ; thus in HClO_4 a concentration of 0.15 *m* indicates already the characteristic form of the absorption curve due to covalent molecules, when the concentration of HClO_4 is about 7 *m*. In ether the same obtains even for a solution of 0.053 *m* of nitric acid, and in hexane the electrovalent form appears to be missing entirely. We shall see below, that this specific influence of the outside forces is in excellent agreement with the theory of the transition from covalency to electrovalency.

Similar conditions obtain for other acids and their derivatives. The sulphate ion, even in supersaturated solutions at 40° C of Na_2SO_4 does not show any selective absorption at all, but an end-absorption only, just at the limit of the quartz spectrograph at about 225 *mμ*. In solution of NaHSO_4 and KHSO_4 in strong concentrations, and in $\text{Na. CH}_3 \text{ SO}_4$ in aqueous solutions a diffuse selective absorption has been found in the region between 300 and 250 *mμ*, whose centre of gravity is difficult to determine accurately. When both bonds become covalent, *i.e.*, in dimethyl sulphate and diethyl sulphate, a similar but more distinct selective absorption obtains, the maximum in the liquid state and in ether solutions lying at about 275 to 270 *mμ*.¹⁷ We did not find any experiments described in the available literature on the absorption of similar substances in the vapour state but since the Raman effect indicates a high percentage of covalent molecules $(\text{H}-\text{O})_2\text{SO}_2$ in aqueous solutions containing about 50% of sulphuric acid ($\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$) we decided to take the absorption of the esters in the liquid state and of H_2SO_4 in the vapour state as criterion of the covalent form. The bands of selective absorption in solution have been found rather late, because their absorption coefficient is 1000 to 5000 times smaller than in the case of the nitrates and necessitates to measure the absorption of the acid in the vapour state with long columns of the absorbing substance. With a tube of 80 cm length and 2 mm vapour pressure we found selective absorption in the vapour of pure H_2SO_4 in the region between 290 and 260 *mμ* with a maximum at about 262 *mμ* resembling the absorption of the organic esters in contradistinction to the absorption of the sulphate ion.

Aqueous solutions of KNO_3 have been measured by v. Halban and Eisenbrand¹¹ and possess a distinct absorption maximum at 375 *mμ*. In



FIG. 1. KNO_3

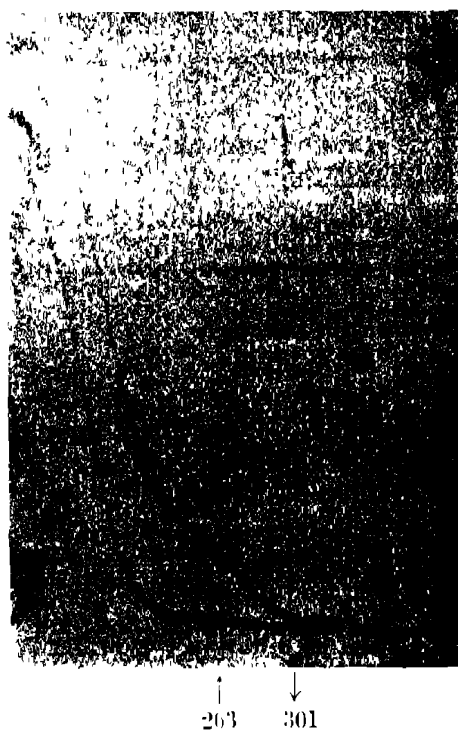


FIG. 2. AgNO_3

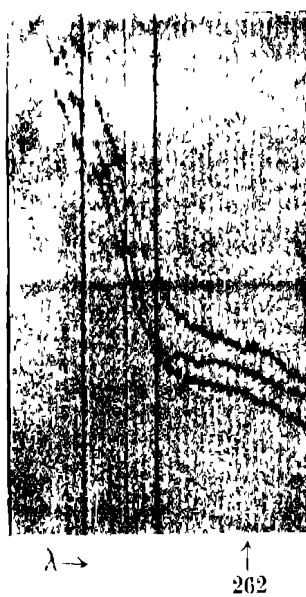


FIG. 3. ZnSO_4



FIG. 4. ZnSO_4

the vapour state¹⁸ the maximum is again shifted towards shorter wave-length, *i.e.*, to $363\text{ m}\mu$ in ethyl nitrite. This difference is, however, very small and it may well be that both maxima are identical, belonging to a photo-dissociation common to the electrovalent and the covalent form, and that the maximum is shifted on account of polarisation in solution.

Experimental.

The substances were heated in porcelain tubes of about 80 cm length in order to obtain clear absorption spectra even with low vapour pressures, *i.e.*, at such low temperatures, where decomposition does not yet take place. The porcelain tube was closed on both ends by heavy brass fittings carrying a quartz window each, which allowed a connection with the vacuum arrangement and were surrounded by cooling spirals. The continuous hydrogen spectrum was used as the source of light and a small Hilger quartz spectrograph as the resolving instrument. Besides the standard lines (Cu arc) on each plate absorption spectra through the empty tube and through the vapour in vacuum were taken with equal times of exposure. These plates were measured by means of a recording microphotometer (see Figs. 1 to 4) and the position of the red wave limits and maxima determined directly on the photometer records.

After having placed the compounds in the absorption tube this was evacuated at room temperature for one to several hours, in order to remove the crystal water. This process was repeated for some hours at various temperatures in the range up to about 100°C . below the melting point of the anhydrous salt. Then the temperature was increased up to the melting point and above it, and the spectra taken.

The results are collected in Table I and Figs 1 to 4 are reproductions of photometer records of KNO_3 , AgNO_3 , $(\text{NH}_4)\text{NO}_3$, and ZnSO_4 . The spectra have been taken under the following conditions:—

Nitric acid, HNO_3 —decomposes easily on heating. At 90°C . the bands of NO_2 can be seen on the plate and with slightly higher temperature also absorption bands of NO appear. The final plates have been taken after replacing the long porcelain tube in this case by a small silica tube of 10 cm. length, varying the vapour pressure at room temperature. The selective absorption appears at 2 mm. vapour pressure and is well developed at 4 mm.

Potassium nitrate (*M.P.* 336°C .).—The first of the two sets of NO_2 bands appears on the plates at the temperature of 475°C . At 360°C . to 375°C . selective absorption obtains which disappears at higher temperatures along with the appearance of the NO_2 bands (Fig 1).

Silver nitrate (*M.P.* 208°.5).—Decomposition becomes rapid from 250° onwards, the selective absorption being well developed at 234° (see Figs. 1 and 2).

Magnesium nitrate—begins to decompose, according to the appearance of the NO bands, already at about 170°, the NO₂ bands appear at about 300°. The spectrum at lower temperatures (165°) shows rather an indistinct selective absorption which is better developed at 280° to 300° C

Cadmium nitrate (*M.P.* 350°)—decomposes very rapidly. At 350° C. the two sets of NO₂ bands are already very strongly developed and fill almost the whole spectrum. The absorption spectrum of the vapour could not be obtained.

Lead nitrate, *Pb(NO₃)₂*—The NO bands begin to appear at about 290°, those of NO₂ at 370°. The selective absorption of the vapour is present at 240° and is still better developed at higher temperatures.

Ammonium nitrate, *NH₄NO₃*—The decomposition of ammonium nitrate occurs first at about 200° C. indicated by the NO₂ bands, and becomes very rapid at about 280° C. The selective absorption is indicated at about 110° C. and well developed at about 240° C. It was rather difficult, to maintain equal illumination, because water vapour was freely condensed on the quartz windows, but the same continuous absorption could be recognised on a great number of photometer records, taken from different plates (Fig. 3)

Sodium nitrate, *Na(NO₂)* (*M.P.* 276°.9).—The decomposition is indicated by the appearance of the two NO₂ band systems, but it appears interesting that also the typical NO bands appear much stronger than in the nitrates. As a matter of fact, these latter bands begin to appear at about 275° C whereas the NO₂ bands are appreciably developed at 380° C. only. At both these temperatures the selective absorption of the salt in the vapour state is already unmistakably present on the photometer record

Sulphuric acid, *H₂SO₄*—is liable to rapid decomposition, when heated in the liquid state. The first SO₂ bands appear at about 110° C., they are fully developed at about 270° C. and the decomposition appears to be almost complete at 400° C. The final plates were taken by placing the acid in a side bulb, and by selecting various vapour pressures without heating it. The selective absorption is well developed on plates, taken with a 80 cm tube and with 2 mm. vapour pressure. It appears, however, as if some SO₂ still was present, because with increasing temperature and pressure not only the red wave limit but also the maximum shifts considerably towards longer waves, between the limits of 290 and 260 *mμ*. We believe that the long wave maxima are produced by the superposition of the absorption of unresolved SO₂ bands and from a careful study of a greater number of plates

and photometer records we think the value of $262\text{ m}\mu$ the most probable one. Similar difficulties occurred in K_2SO_4 and these two values are therefore less reliable than those of other compounds.

Potassium sulphate, $\text{K}_2(\text{SO}_4)$ (M.P. 1067°).—The short wave SO_2 bands appear at 775° , the first of the near ultra-violet bands at 830° . The selective absorption of the salt is just indicated at about 600° and very well developed at about 800° . Here similar difficulties were encountered as in H_2SO_4 , and the value of $254\text{ m}\mu$ appears to be the most probable one for the maximum.

Silver sulphate, $\text{Ag}_2(\text{SO}_4)$ (M.P. 660°).—The first weak indications of the SO_2 bands appear already much below the melting point at about 180° and the decomposition becomes rapid at about 300° to 350° . Selective absorption of the vapour obtains from 160° onwards.

Zinc sulphate—Decomposition obtains from 550° onwards and becomes very rapid from 800° onwards. The continuous absorption of the salt can be recognised from about 600° onwards, together with that of traces of SO_2 at longer wave-lengths (Fig 4).

Ammonium sulphate—is very unstable and decomposes easily, so much so that already near the melting point the near ultra-violet SO_2 bands cover the region of the probable selective absorption. We have not been able to obtain a plate on which the selective absorption could be determined with complete certainty but some plates indicate that $(\text{NH}_4)_2\text{SO}_4$ behaves similar to K_2SO_4 .

The Structure of Nitrates and Sulphates in the Vapour State and the Transition from Covalency to Electrovalency.

From Table I, where the results are summarised, it can be seen, that the figures are more or less the same for all the nitrates and all the sulphates respectively. Whether the individual differences from salt to salt are genuine or not is difficult to say at the present moment. It has been pointed out in earlier papers³ that for continuous absorption spectra the position of the red wave limit, and to a smaller degree, that of the maximum depends on temperature and vapour pressure, and these two factors vary very much in these experiments for the different salts. For these salts the accurate determination of the wave-lengths of the maxima becomes even more difficult, because the vapour pressure obtainable without decomposition, is rather low and the maxima themselves naturally rather flat and further experiments with even longer absorption cells and higher resolving power are necessary. It can be seen, however, that the absorption of the sulphates generally lies on the long wave side of the nitrates and that in both cases

TABLE I.

	Beginning of Absorption	Maximum	Retransmission	Remarks
	λ ($m\mu$)	λ ($m\mu$)	λ ($m\mu$)	
$(\text{NO}_3)^-$		302		Nitrates in dilute aqueous solution ^{11,12}
(HNO_3)		~ 265		Nitric acid in hexane ^{11,12}
$\text{C}_2\text{H}_5\text{NO}_3$		~ 270		Ethyl nitrate in hexane ^{11,12}
$\text{C}_2\text{H}_5\text{NO}_3$		~ 265		Vapour ¹³
HNO_3	298	262	252	Vapour, present paper
KNO_3	308	267	252	" " "
AgNO_3	301	263	251	" " "
$\text{Mg}(\text{NO}_3)_2$	294	270	257	" " "
$\text{Pb}(\text{NO}_3)_2$	292	268	252	" " "
NH_4NO_3	299	262	252	" " "
$(\text{NO}_2)^-$		375		KNO_2 , dilute aqueous solution ¹¹
$\text{C}_2\text{H}_5\text{NO}_2$		363		Ethyl nitrite, vapour state ¹³
NaNO_2	301	271	254	Vapour, present paper
SO_4^{2-}		< 225		Sulphates, in dilute aqueous solution, max probably in Schumann-region ¹⁷
$(\text{CH}_3)_2\text{SO}_4$		~ 275		Dimethyl sulphate, homogen. liquid ¹⁷
$(\text{C}_2\text{H}_5)_2\text{SO}_4$		~ 270		Diethyl sulphate, homog. liqu. and sol in ether ¹⁷
H_2SO_4	285	262	254	Vapour, present paper
K_2SO_4	293	258	254	" " "
Ag_2SO_4	300	265	250	" " "
ZnSO_4	294	269	242	" " "

the region of selective absorption is close to that of the organic esters but very different from that of the free ions in solution. We conclude, that inorganic sulphates and nitrates are covalently bound in the vapour state. For the nitrites this is not yet certain, but probable.

To our mind this result is by no means surprising. The experiments of Franck and his collaborators¹ have shown that a transition from covalent to electrovalent linkage exists for the same molecule under different experimental conditions. Thus AgCl, well known to dissociate into Ag⁺ and Cl⁻ ions in solution and in the fused state, possesses a covalent linkage in the vapour state according to its continuous absorption spectrum and its band spectrum in emission. Similarly HCl, HBr, and HI are covalently bound in the vapour state according to their absorption spectrum, their Raman effect and the value of their dipole moments.¹⁸ There are only two possibilities to explain these results. We have either to assume the existence of a particular class of molecules, which dissociate adiabatically into ions but are not made up of ions in their ground state, or, we assume that the bond may change from the covalent to the electrovalent character. In order to leave both ways open, Franck put forward the terminology of atomic binding and ionic binding, mentioned above. If the first explanation would be found valid, the terms electrovalent and covalent could be preserved with their chemical meaning and could denote compounds, which dissociate into ions or which do not respectively. If the second explanation holds, any bond would be either electrovalent or covalent at a particular moment, the two terminologies becoming identical, but the nature of the same bond would be found different under different conditions. From the point of view of wavemechanics both explanations are possible.¹⁹ The latter one, *i.e.*, the transition from covalent to electrovalent linkage would find its analytical representation in an increasing difference of the normalising factors of the bonding wavefunction, *i.e.*, in an increasing dissymmetry of the molecular fields. The first explanation can be described wave-mechanically by hybridisation of several wavefunctions. The term hybridisation is used with different meanings in literature, and the type of hybridisation discussed here obtains, when the two potential curves involving ions and atoms, come near enough and perturb each other at such internuclear distances as really prevail in the completed molecule. An intersection of the ionic and the atomic curve at large internuclear distance, which was believed sometime ago to explain such cases, is not qualified to bring about a hybridised ionic-*cum*-atomic bond. But the theory itself is unable to decide, the order of magnitude for the dissymmetry of the fields or the energy difference of the electronic levels at the minimum position of the $u : r$ curves, necessary for the explanation of these phenomena. Experimentally, however, it can be said, that a hybridisation would mean a perturbation of the vibrational levels and it should be possible to recognise it in the band spectrum. Neither the bands of AgCl indicate a perturbation owing to the

hybridisation of the ionic and atomic potential curves, nor the bands of BeO, MgO, etc. for which hybridisation of the s and p terms was supposed for similar reasons. In all such cases the spacing of the vibrational levels is quite regular.

On the other hand it is clear, that the transition from covalency to electrovalency depends to a very high degree on external conditions. According to conductivity and Raman effect, AgCl is electrovalent already in the melted state, but HCl remains covalent in the liquid state in the absence of water and even in solution in solvents of smaller dipole moment. Thus the expected experimental evidence for the explanation of hybridisation is missing but that for the influence of external forces exists indeed and we believe, therefore, that the second explanation holds. We identify the definition of covalency and atomic binding on the one hand and of electrovalency and ionic binding on the other hand, but assume, that the nature of the bond may change for the same molecule under different conditions.

The influence of external conditions and forces on the nature of the bond may easily be seen from the Franck-Condon diagram. Here the different effects of polarisation can be considered by introducing the changes of energy produced by them. Fig 5 contains the $u.r$ curve of KCl. The ground state of this electrovalent molecule dissociates into $K^+ + Cl^-$.

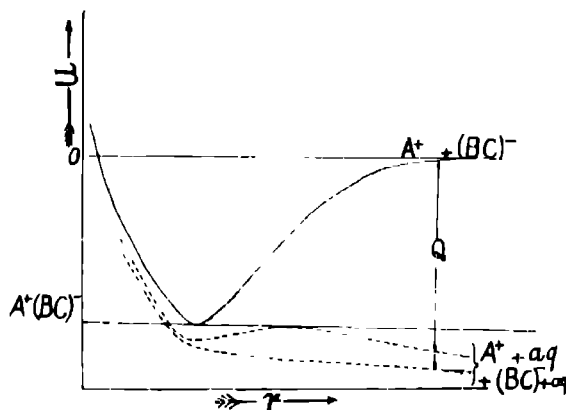


FIG 5.

The level of the separated unexcited atoms $K + Cl$ lies 0.6 volts (ionisation potential of K minus electronic affinity of Cl) below it and a flat repulsive curve originates from it, as can be seen from the red wave limit of its absorption spectrum in the vapour state. The thermochemical energy of formation $(K^+ Cl^-) \leftarrow K + Cl$ is 4.5 volts, the adiabatic dissociation energy $(K^+ Cl^-) \rightarrow K + Cl$ is 5.1 volts. The energy of hydration is for the K^+ ion about 93 K.cal./mol., for the Cl^- ion about 89 K.cal./mol.,²⁰ together about 7 volts. The hydration energy of an undissociated electrovalent molecule $(K^+ Cl^-)$ is of course not known, but it is clear, that the field outside

such a molecule, in which the changes are counterbalanced, is much weaker, than that surrounding the separated ions. As a matter of fact, the dissociation of the molecule in solution proves, that the curve involving the separated hydrated ions ($K^+ + aq$) + ($Cl^- + aq$) is a repulsive one. The further question, whether a labile minimum position remains in the neighbourhood of the internuclear distance of the gaseous molecule ($K^+ Cl^-$) is of no interest here. It can be seen, however, that the level of the separated *hydrated* ions lies 1.9 volts below the ground level of the molecule. Almost the same obtains for $AgCl$ in spite of this molecule being covalently bound in its ground state. The ground level and the excited level possess a dissociation energy of 3.1 and 0.3 volts respectively²¹ according to its band spectrum,[†] the energy of

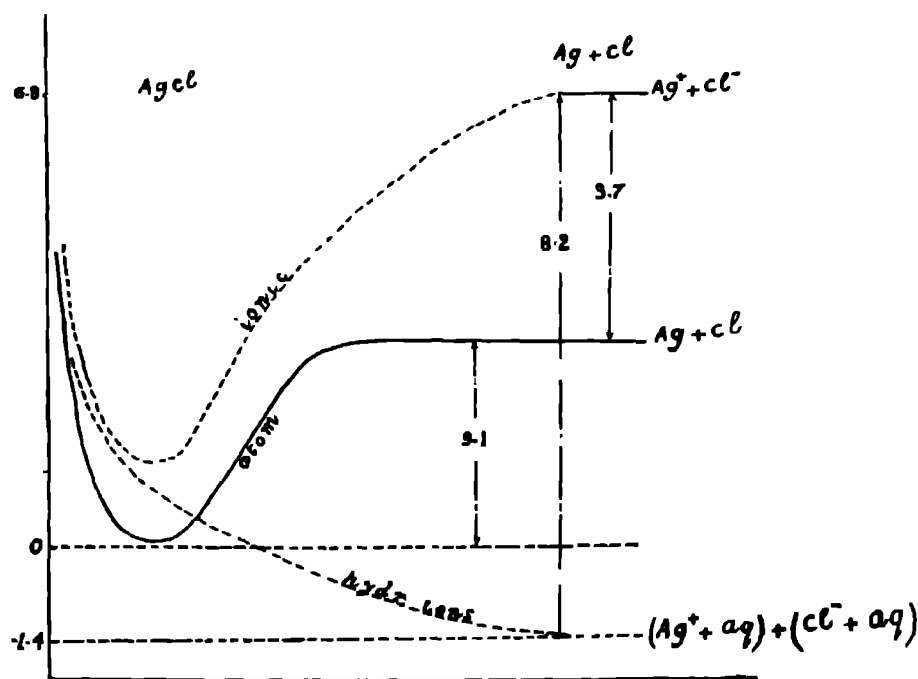


FIG. 6.

† Ag in the term $d^0s^2 \ ^2D$ as dissociation product of the initial level was originally suggested by Brice, but such a term, about 19 volts above the ground state, is not yet known in the spectrum of Ag . One of us (R. Samuel, "Absorpt. Spectr., etc", ref 2) has suggested another possibility, because the extrapolation from the Ag^+ spectrum would give 48 volts instead of 1.1 volts. The 2D term is however known in the Cu spectrum where it lies 138 volts above the ground state 2S and since the ionisation potential of Cu (7.68 volts) is slightly higher than that of Ag (7.54 volts), the term value of 2D will be indeed very near to 1.1 volts. It appears that the extrapolation from the spectrum of the ion which gives good results for the extrapolation, i.e., of the anomalous terms of the earth alkali metals (cf. W. Grotrian, "Graph Darstellung, etc", Berlin, 1927) cannot be applied to such configuration involving an excitation of an electron of the closed d^{10} configuration. The band spectrum of AgO (F. W. Loomis and T. F. Watson, *Phys. Rev.*, 1935, 48, 280) confirms Brice's interpretations of the dissociation of $AgCl$.

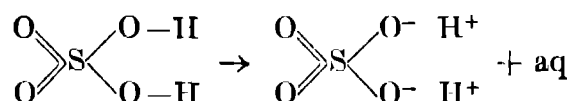
excitation of the molecule being 3.9 volts. But the level of the separated ions lies in this case much higher, about 3.7 volts above that of the normal atoms, because the ionisation potential of Ag is much greater than that of K. In spite of this, the level of the *hydrated* ions becomes again the lowest one of the whole system, the hydration energy of Ag^+ being 100 K.cal./mol.²⁰ that of Ag^+ *plus* Cl^- being 8.2 volts. The level of $(\text{Ag}^+ + \text{aq}) + (\text{Cl}^- + \text{aq})$ therefore lies not only 4.5 volts below that of $\text{Ag} + \text{Cl}$ but also 1.4 volts below the ground state of the covalent gaseous molecule (AgCl). Hence the curve involving the level of the separated hydrated ions intersects that of the ground state of the covalent molecule and becomes a repulsive one. The actual position of the ionic curve is not known, but since the radius of Ag^+ is slightly smaller than that of K^+ and its polarisability greater it will possess an adiabatic energy of dissociation of 5 to 6 volts, as indicated in Fig 6. The hydration energy of the covalent molecule will be much smaller, of the order of a few K cal./mol, and is entirely neglected here. These considerations make the mechanism of the transition from covalency to electrovalency perfectly clear. It occurs on account of the additional energies supplied by the interaction with surrounding molecules or ions in the liquid state, the energies of solvation or hydration in solutions, the lattice energy in the crystal, and these will be big enough, when the minimum of the ionic curve is near to that of the covalent potential curve, which forms the ground state of the molecule. This condition, as can be seen from a comparison of Figs. 5 and 6, depends mainly on the position of the level of the separated ions with respect to that of the separated atoms. The changes in the adiabatic energies of dissociation are much smaller but those introduced particularly by the variation of the ionisation potential of the positive partner. Therefore the difference, "ionisation potential *minus* electronic affinity" determines roughly, whether such a transition from covalency to electrovalency is possible or not. Indeed, Samuel and Lorenz²² could show, that a great number of chemical phenomena as conductivities, hydrolysis, the character of an hydroxide as acid or base a.o, which are intimately connected with the transition from covalency to electrovalency, follow exactly this difference throughout the periodic system. In reality the molecule is rigorously homopolar, when the sum of the energies for all the electrons of the bonding orbital is equal for either of the nuclear fields, the polarity of the molecule is measured by a comparison of the sum of ionisation potential *plus* electronic affinity of both the atoms. But it is sufficient to compare either the ionisation potential or the electronic affinity because both change in the same sense.¹⁹ It is of course possible to consider the reverse process, the transition from electrovalency to covalency in a similar

manner, *e.g.*, by the theory of deformation of Fajans. To our mind, however, the above manner appears to be more satisfactory from a logical point of view and also to be a closer approach to reality. This can be seen from the fact, that in the sub-groups of the periodic system the transition from covalency to electrovalency always occurs easier with molecules formed by the middle element, *e.g.*, Ag, Cd, In, than for those formed by *both* their neighbours Cu and Au, Zn and Hg, Ga and Tl.²³ In a series like Zn, Cd, Hg, those properties, which form the parameter of transition in the theory of deformation like the ionic radius (0.83, 1.03, 1.12 A.U.) and the polarisability of the ions (0.29, 2.44, 5.05) form a monotonous series, whereas the ionisation potential shows indeed a minimum for the middle element (first ionisation potentials = 9.4, 9.0, 10.4, second ones = 17.9, 16.8, 18.7 volts respectively for Zn, Cd, Hg).

The above considerations support the point of view taken up in this paper ; such a transition is possible in the same molecule under different experimental conditions and therefore the terms of ionic and atomic binding and electrovalency and covalency respectively may well be identified. From the absorption spectra of diatomic halides Franck and his collaborators had concluded, that those of H and Ag are covalently bound in the vapour state, those of the alkali metals Na, K, Rb, and Cs indicating electrovalent bond. Since H and Ag possess a high ionisation potential, the alkali metals a low one, we expected a similar difference in the case of nitrates and sulphates; and, as far as the homogeneous acids are concerned, covalency was already established by the Raman effect. This is supported by experiments of Butkow²³, which show that triatomic halides are covalent in the vapour state like those of Zn, Cd and Hg, with high ionisation potential, but electrovalent, if the ionisation potential is low, as in those of Pb. But the experiments reported here show, that in this case even the alkali salts possess a covalent bond in the vapour state. This evidently is due to the electronic affinity of the nitrate and sulphate ion. Its exact value is not known, but it is clear, that it will be smaller in such a complicated system than for a simple halide ion. The above experiments indicate that the difference between the electronic affinity of the halides and these groups is considerable and greater than what could be expected.

As the absorption spectra in the vapour state indicate covalent bond between the metal and the oxygen atom for the nitrates and sulphates, it appears, as if this phenomenon is rather common and we expect most of the simple inorganic salts (as distinct from genuine complex salts) to behave similarly. Further experiments on this point are in progress. In current literature the sulphate or nitrate ion is often described by a formula

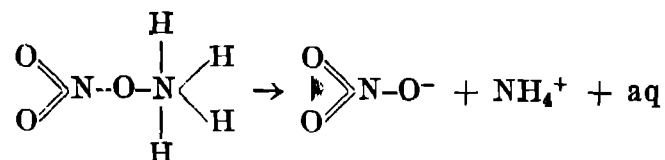
$[\text{SO}_4]^-$ and $[\text{NO}_3]^-$ indicating that such molecules belong to the same class of compounds as Werner's complex salts. It has been pointed out²⁴ that according to spectroscopical results several classes have to be distinguished among the complex salts, as the term is used to-day, and quite different mechanisms of linkage are responsible, *e.g.*, for the existence of NO_3^- , $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, each of them representing a different type of chemical union. Werner himself was the first to assume that the sulphate and nitrate ion are really complex salts, but, while it can be understood that he tried to extend his new theory of co-ordination as far as possible, it should not be overlooked, that the arguments put forward by him do not hold any longer. As a matter of principle he did not want to make use of particular and definite ideas on the structure of atoms and did not want to ascribe different states of valency to the same atom. To-day there is not the slightest difficulty to explain the tetra and hexavalency of sulphur on the basis of the configuration $s^2 p^4$ of the sulphur atom, the s -electrons being active in the hexavalent, but inactive in the tetravalent state. Again the experimental facts cited by Werner, do not warrant in themselves, the assumption of a co-ordinate bond for *e.g.* SO_4^{2-} . The hydrogen atoms are easily substituted in H_2SO_4 , it is true, but this does not prove that they are bound in the second sphere of a complex, because the same is true for the hydroxyl group too, as can be seen from reactions like the combination of H_2SO_4 and HCl to give SO_2Cl_2 . Indeed just for such cases Werner ultimately had to assume a rearrangement into "ordinary valence compounds"²⁵. To our mind the covalent bond in the vapour state indicates clearly that a description by the older structural formulæ



are a close approach to reality, showing that such compounds can exist with the same number of valencies once in the covalent and once in the electrovalent state. Whether the two kinds of oxygen atoms, bound with a single and a double bond in the covalent form still can be distinguished in the free ion or not is a different question. Electronic configuration for both cases are conceivable and a definite answer on this point cannot be given at this moment.

Particular interest attaches itself to the spectrum of ammonium nitrate which does not form an exception but absorbs similarly to the other nitrates. Sidgwick²⁶ has introduced the "covalency maximum" of four for nitrogen on the basis of the Octet Theory and quotes the ammonium salts as examples, showing that the fifth bond of nitrogen cannot be covalent. Since $\text{NH}_4 \cdot \text{NO}_3$

in the vapour state absorbs like $C_2H_5.NO_3$ and not like the free nitrate ion in solution, there appears to be no other possibility but to describe it by a formula



according to which nitrogen possesses 5 covalent bonds in the vapour state and the bond with highest polarisation becomes electrovalent on account of the external energies of the lattice or of hydration. As to the nitro-group, it has been proposed to avoid the pentacovalency by the assumption of a resonance bond. For such a system, wavemechanical calculation becomes rather complicated, but for a similar case, *i.e.*, the $(\text{HF}_2)^-$ ion, quoted often along with the nitro-group in this connection, it can be seen at once, that a resonance linkage does not exist. For this purpose we assume for this ion a model, consisting of two F^- ions, bound together by a proton. This model corresponds exactly to that of H_2^+ , made up of two H^+ ions, bound by a single electron, as it is used for wavemechanical purposes, only with the reverse signs. Therefore the results of the corresponding calculation²⁷ may be applied, and it can be seen, that the system $(\text{FHF})^-$ indeed possesses a stable minimum position, like H_2^+ ; but because the proton is about 1840 times heavier than the electron, the dissociation energy of HF_2^- would be 1840 times greater and the internuclear distance ($\text{F}-\text{F}$) 1840 times smaller than the corresponding dissociation energy and distance in H_2^+ . If a physical meaning is at all attached to such a calculation, it cannot be anything else but that of an "united atom". At the internuclear distance of the $(\text{HF}_2)^-$ ion, the system accordingly does not possess a stable minimum position, produced by wavemechanical interaction.

On the other hand, the existence of this ion in solution is readily explained by electrostatic attraction between the dipole of non-dissociated HF molecules and F^- ions and such an explanation makes it easily understood, why such phenomena are always confined to the elements with smallest atomic dimensions, as has been pointed out elsewhere²⁸. Also in this case ions like $(\text{HCl}_2)^-$ and $(\text{HBr}_2)^-$ do not exist. Resonance linkage is doubtless present in aromatic compounds, but because it accounts here for the particular aromatic properties, it is all the more probable *a priori*, that it does not exist in non-aromatic molecules, and it is therefore our view, that the nitro-group has to be conceived as derived from a pentacovalent nitrogen atom. As to the ammonium part of $\text{NH}_4.NO_3$ in the vapour state, there is little doubt, that nitrogen is pentacovalent according to the absorption

spectrum and this agrees with recent indications of a pentacovalency of N in solutions of tetra-alkyl ammonium salts¹⁴ and certain evidence for the existence of NF_5 .²⁹

The pentacovalency of nitrogen, indicated for ammonium nitrate in the vapour state, is also of interest, because Mulliken³⁰ uses the existence of the NH_4 ion with not more than 4 covalent linkages as a general argument, to interpret the method of molecular orbitals by means of the identification of non-promoted and bonding electrons as a theory of valency in which the single electron possesses bonding power. The above results favour directly an electron pair-bond theory of valency, as suggested elsewhere,^{6,28} and may be added to the increasing spectroscopical evidence, which supports this view.

Discussion of Possible Photo-dissociation Processes.

The correlation of the maxima observed in the vapour state and their red wave limit to particular processes of photo-dissociation meets with two difficulties. Firstly, as in all experiments concerned with continuous absorption spectra, it is difficult to determine the red wave limit belonging to the vibrationless molecule. As discussed elsewhere in some detail,³ the observed red wave limit will give too large values of the dissociation energy if the number of absorbing molecules is not sufficient to make the absorption complete, and it will give too small values, when a considerable percentage of the absorbing molecules is already excited to higher vibrational levels of the ground state, the number of collisions being increased by increased pressure or temperature. In this particular case the vapour pressure of the anhydrous salts is particularly small and we have tried to account for that by an absorption tube of unusual length. The difference between the observed maxima and the red wave limit is generally about 300 A.U., and according to experience gained with other substances, such a figure should give a value not too much different from that of the vibrationless molecule. We believe, that the dissociation energies obtained from the beginning of the continuous absorption will be of the right order of magnitude, and, if anything, rather too great than too small.

The second difficulty is the following: all inorganic nitrates in aqueous solutions of low concentration show the same selective absorption $\lambda_{\text{max}} = 302 \text{ m}\mu$, which evidently has to be correlated to some process of photo-dissociation of the NO_3^- ions. Nitric acid in highly concentrated aqueous solutions, in non-dissociating solvents, organic nitrates in solution are measured as homogeneous substance, and all inorganic and organic nitrates in the vapour state exhibit the same selective absorption with its centre of gravity at about 265 to 270 $\text{m}\mu$; this evidently has to be correlated to some

photo-dissociation of the covalently bound NO_3 group, since otherwise the above figure could not remain rather constant for so different partners as Na, H and C_2H_5 . Hence the transition from electrovalent to covalent linkage brings about a change in the dissociation process in such a way, that the dissociation energy is *increased*. In a similar way there exists some dissociation process* for the sulphate ion with a red wave limit at $220\text{ m}\mu$ or below. Organic sulphates in the liquid state or solution, sulphuric acid and inorganic sulphates in the vapour state all possess a selective absorption $\lambda_{\text{max}} = 270$ to $290\text{ m}\mu$. Similarly this has to be ascribed to a dissociation process concerning the covalently bound SO_4 group, and the transition from electrovalency to covalency in this case brings about a change of the dissociation process which *decreases* the dissociation energy. But in both the groups, NO_3 and SO_4 in covalent linkage we have a central atom bound to oxygen atoms according to its maximal number of valencies and hence we should not expect dissociation processes, which are vastly dissimilar.

It could be possible to account for the above difference in behaviour, assuming that the spectra due to the negative nitrate and sulphate ions correspond to a dissociation process concerning not an atom but the superfluous electrons and are correlated to the electronic affinity of these ions. But then the electron affinity of e.g., SO_4 would be greater, not smaller than that of iodine. Moreover, Krishnan and Guha,⁸¹ have made it probable, that the two selective absorptions of the nitrate ions belong indeed to the two processes $\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}(^3\text{P})$ and $\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}(^1\text{D})$. Since they have taken the value of the red wave limit from absorption spectra in solution, the agreement between thermochemical determination and this value is not a definite proof, the beginning of the photo-dissociation of the free ions in the state of minimum vibration probably lies at higher energy values than they suppose, the potential curve of the repulsive state which is the final level of this transition, running rather steep towards decreasing internuclear distance. That the red wave limit lies at higher values of the absorption coefficient than those selected by Krishnan and Guha, can be seen from a comparison of the absorption spectra of many compounds in the vapour state and in solution, but nevertheless, the above correlation is made quite plausible, because the energy difference between the two maxima of NO_3^- , i.e., 302 and $193\text{ m}\mu$ is about 2.3 volts in fair agreement with the excitation energy 1.9 volts of $\text{O}(^1\text{D})$, and the energy difference of the maxima is always more reliable than that of the red wave limits. They calculate for the dissociation process $\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}(^3\text{P})$ the energy difference of about 83 K.cal./mol. in dilute aqueous solution.

As to the absorption spectra of the covalent molecules, it is by no

means possible definitely to decide on the photo-dissociation connected with them. The known energies of formation of acids and salts cannot be used to calculate the atomic heat of formation, because they all refer to measurements in the crystalline state or in solution, in which these corresponds possess an electrovalent bond. Furthermore, it is not possible to calculate the atomic energy of formation from these values by means of some cycle, because a number of the necessary quantities, *e.g.*, the electron affinity of NO_3 are not known.

Atomic energies of formation of similar covalent molecules are, however, available for organic esters of nitrous and nitric acids, *i.e.*, for ethyl nitrite and ethyl nitrate, which can be calculated from the known heats of combustion. These are for the gaseous molecules 324 and 334 K cal/mol. respectively. When calculating the atomic energies of formation and deducting one from the other, again all quantities cancel out with the exception of $\frac{1}{2}\text{D}(\text{O}_2)$ and hence the dissociation process $\text{C}_2\text{H}_5\text{O.NO}_2 \rightarrow \text{C}_2\text{H}_5\text{O.NO} + \text{O}$ represents an energy of $10 + 59 = 69$ K cal/mol. The same value obtains for the anhydride of nitric and nitrous acid. The energies of formation from the elements are $Q(\text{N}_2\text{O}_5) = -1.2$, and $Q(\text{N}_2\text{O}_3) = -22$ K.cal./mol and give the atomic energies of formation $\text{D}(\text{N}_2\text{O}_5) = 463$ and $\text{D}(\text{N}_2\text{O}_3) = 325$ K.cal./mol or 69 K cal./mol. for the dissociation process $\frac{1}{2}\text{N}_2\text{O}_5 \rightarrow \frac{1}{2}\text{N}_2\text{O}_3 + \text{O}$.

The dissociation process $\text{SO}_4^- \rightarrow \text{SO}_3^- + \text{O}(^3\text{P})$ may be considered in a similar way. The following figures in Table II are obtained by adding half of the dissociation energy of O_2 to the heat of formation $Q(\text{M}_2\text{SO}_4)$ of the sulphates from the elements in aqueous solutions and deducting the corresponding heat of formation of the sulphites $Q(\text{M}_2\text{SO}_3)$.—

TABLE II.

M =	Na	K	NH_4	Mg^*
$Q(\text{M}_2\text{SO}_4)$	328	334	280	302
$+ \frac{1}{2}\text{D}(\text{O}_2)$	59	59	59	59
$- Q(\text{M}_2\text{SO}_3)$	264	275	214	240
$\text{SO}_4^- \rightarrow \text{SO}_3^- + \text{O}$	123	118	125	121

* These figures refer to the solid state

The atomic heat of formation of SO_2 has been calculated to 247, that of H_2O to 217 K.cal./mol. The heat of solution of $\text{SO}_2 + \text{aq}$ is about 6 K cal./mol., and the atomic heat of formation of H_2SO_3 in dilute aqueous

solutions comes to about 470 K.cal./mol. The heat of formation from the elements of 214 K.cal./mol. of sulphuric acid in dilute aqueous solution gives an atomic energy of formation of 607 K.cal./mol., and the dissociation energy of the process $\text{H}_2\text{SO}_4 + \text{aq} \rightarrow \text{H}_2\text{SO}_3 + \text{aq} + \text{O}$ is about 137 K.cal./mol. This value is slightly higher than that obtained from the salts, and the difference may be due to different degrees of dilution. It is, however, not impossible, that sulphuric acid behaves slightly different from the sulphates, because also in the vapour state the spectrum of the acid is slightly shifted against that of the salts. For the splitting off of a neutral oxygen atom from the free SO_4^{2-} -ion we may take an energy value of roughly 125 K.cal./mol. This corresponds to a wave-length of $227m\mu$. The absorption of the sulphate ion indeed begins in this region and appears to be correlated to this process.

For covalent molecules of this type the corresponding energies cannot be calculated, because reliable values of energies of combustion of organic esters of sulphuric and sulphurous acids are not known. For the anhydrides of the acids from the values $Q(\text{SO}_3) = 92$ and $Q(\text{SO}_2) = 71$ K.cal./mol. by the addition of $\frac{1}{2} D(\text{O}_2)$ a value of 80 K.cal./mol. is obtained for the splitting off of an oxygen atom in the gaseous state. In analogy to ethyl nitrate and ethyl nitrite this value may be taken as valid for the organic esters provisionally.

In other words, the energy of this dissociation process is reduced from 125 K.cal./mol. for the hydrated ion to 80 K.cal./mol. for the gaseous covalent molecule. While the first value agrees with the beginning of the absorption spectrum in aqueous solution, the latter one corresponds fairly well to the red wave limit of sulphates and sulphuric acid in the vapour state. The mean of the above observations is about 90 K.cal./mol. and the difference of 10 K.cal./mol. is not significant in any way, because, firstly, the vapour pressure naturally was very small and, secondly, the upper repulsive potential curve runs parallel to the abscissa of the internuclear distance of the $U : r$ diagram only in rare cases. The above figures explain why the absorption is shifted towards longer wave-length in the transition from electrovalency to covalency and it appears, as if the beginning of the absorption has to be correlated to the dissociation of an unexcited O atom in both cases.

For the nitrates, however, the difficulty which was mentioned above remains, *i.e.*, that the absorption is shifted to shorter wave-length by the same transition from electrovalency to covalency contrary to the behaviour of the sulphates, while the energy of the dissociation process is decreased from 83 to 69 K.cal./mol. respectively, in a similar manner, as in the case of the sulphates. This may be explained, of course, by a different slope of

the repulsive curve. We know indeed a large number of polyatomic molecules, *e.g.*, the type CH_3Cl , where the energy of dissociation, measured optically, is much too large on account of the steepness of the upper potential curve. It should be borne in mind, that the energy differences measured by the red wave limit of the continuous absorption spectrum in reality are energies of electronic excitation of the molecule, which depend on the potential curve not only of the ground state but of the final state as well. But still, this disagreement is by no means satisfactory, particularly considering the good agreement obtained for sulphates, and since various other photodissociation processes are possible, a definite correlation of the red wave limit of the absorption in the gaseous state may be reserved for a time, till more experimental data of other inorganic salts are available

Again the second red wave limit, *ie*, the point of retransmission, cannot be explained satisfactorily at present. The energy difference between the first and second red wave limit is about 0.8 volts for the nitrates and about 1 volt for the sulphates, and these values do not agree either with the term difference $^1\text{D} - ^3\text{P}$ of oxygen or with its triplet separation. The difference between the absorption maxima which is not yet known, would give clearer results and also the discussion on this question has to be postponed

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Absorption Spectra & Linkage of Inorganic Nitrates & Sulphates 511

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LIPINS OF FENUGREEK (*TRIGONELLA FOENUM GRAECUM*.)

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FENUGREEK, extensively cultivated throughout India and Egypt, forms an essential constituent of the Indian, Arab and Egyptian dietary. Data relating to the area under its cultivation in India are not available but statistics show that the seeds are exported to the extent of about 770 tons per annum valued at about 2 lakhs and a half—(1927), principally to Arabia, Egypt and Italy. Its nutritive value has long been recognised, aqueous extracts of the seed being commonly administered to anæmic and ricketty children. Dr Blum (1927) states that fenugreek can be employed as a substitute for cod liver oil in cases of lymphatism, scorfula, rickets, anæmia and debility following infectious diseases or neurasthenia as well as in gout and diabetes in which it may be combined with insulin.

The seeds are valued for their tonic, astringent, emollient and aphrodisiac properties and recently their dietetic value is being more widely accepted. Andre (1932) reports an augmentation in the weight of adults (1.5 to 4 kg.) in 1–2 months by administering the powder to them in 2–3 gm. doses before food. Fenugreek is given to women after parturition in the form of powder or a decoction sweetened with sugar, for re-establishing original weight and improving lactation. It constitutes an essential ingredient of pills and powders administered for the treatment of diabetes mellitus; it also acts as a safe nutrient in cases of diabetes.

Reutter (1927) has noted the presence of several bases such as choline, trigonelline, methylamine, neurine and betain, which possibly result during the hydrolysis of the lipins associated with the grain. The seed contains about 7 per cent. of a fixed oil (1919), bright yellow in colour, with a characteristic odour and taste. Wunschendorff (1919) has found that the oil possesses an iodine value of about 137, contains 6.25 per cent. of a lecithin and has a phosphorus content of (P_2O_5) 0.55 per cent. In a further communication (1919) he has reported the presence of a saponin, readily soluble in water and easily hydrolysed by dilute acids yielding dextrose.

Jahns (1885) isolated an alkaloid, trigonelline, from the seeds by exhausting them with 70 per cent. alcohol. 0.14 per cent. of a light brown neutral volatile oil possessing the distinct odour of seeds has been described (1903). The preliminary study of the proteins of the seed has been conducted by Wunschendorff (1919) who has isolated 25 per cent. of a globulin, 20 per cent. of two albumins and 55 per cent. of an alkali soluble nucleoprotein having a specific laevo rotation of $[\alpha]_D = -97.7^\circ$. More recently, the albumins and globulins have been examined in greater detail by Sreenivasa Rau and Sreenivasaya (1932) while a preliminary examination of the prolamin, "Helbin", has been conducted by Hassan and Basha (1932), a more complete study of which has been carried out by Sreenivasa Rau, Sastri and Narayana (1933).

The mucilage to which the emollient properties are attributed, is described to be a silico-phosphoric acid ester of mannogalactan (1932) in contradiction to the previous finding of Bourquelot and Herissey that it is a mannogalactan (1900). A critical examination of this question by Hariharan and Sastri (1933) has revealed that the mucilage is a simple mannogalactan.

It will be observed from the foregoing review of the work done on Fenugreek that there have been no systematic studies on the lipins of the seed to which the reputed tonic properties of the seed may largely be due. A detailed investigation of lipins has accordingly been undertaken in our laboratories and the present communication deals with the methods employed in the isolation, fractionation and chemical characterisation of the lipins.

Experimental.

The seeds, on crushing, separate roughly into two portions, a yellow flour which is easily powdered and a residue consisting of the snow-white gelatinous endosperms which cannot be ground. The yellow meal has a nitrogen value of 4.54 per cent. while the endosperm fraction, constituting the source of the mucilage, if carefully separated, is found to contain practically no nitrogen. Table I gives the proximate composition of the yellow meal in percentages of moisture-free material.

TABLE I.

Ether extract	98% alcohol extract	70% alcohol extract	Crude protein $N \times 6.3$	Total Ash	Total P	Total S	Starch
8.1	4.9	11.2	29.9	3.5	0.62	0.003	2.1

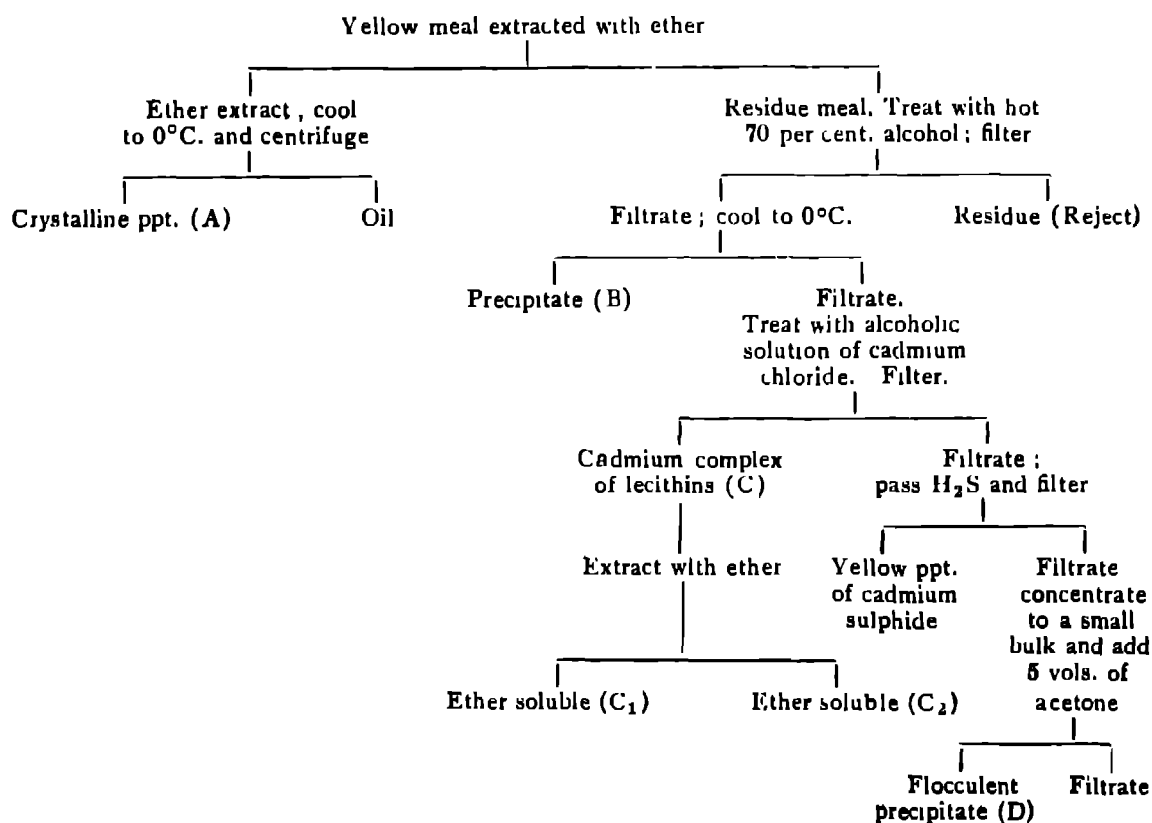
The nitrogen and phosphorus values of the ether extract are 0.38 and 0.52 per cent. respectively while the corresponding values for the alcohol

extract are (N) 1.10 and (P) 1.51 per cent, about thrice as high. About 3 per cent. of the total nitrogen and 30 of the total phosphorus of the yellow meal are extracted by successive treatments with ether and alcohol, while direct treatment with 70 per cent. alcohol, however, yields about 5.8 and 60 per cent of the total nitrogen and phosphorus respectively.

The ether extract of the meal consists of a viscous semi-drying oil, golden yellow in colour. On cooling the oil deposits a white crystalline substance (A) which can be recovered by centrifuging and purified from the oil by washing with acetone in which the crystals are insoluble. The substance is sparingly soluble in ether and in absolute alcohol from which it could be recrystallised; it is freely soluble in water and also in 70 per cent. alcohol from which it can be precipitated by adding 10 volumes of acetone. The purified product contains both nitrogen and phosphorus and represents the oil soluble phospholipin.

The ether extracted meal, on treatment with hot 70 per cent. alcohol, yields a clear light yellow solution which on cooling to 0° C. deposits a white precipitate (B) which can be filtered off and washed with cold alcohol. The filtrate is concentrated to a small bulk and treated with an alcoholic solution of cadmium chloride, to precipitate the true lecithins as double salt.

TABLE II.



The mixture is centrifuged to recover the cadmium complex (C) and the centrifugate treated with hydrogen sulphide to remove excess of cadmium as sulphide which is filtered off. The filtrate is concentrated to a small bulk and 5 volumes of acetone added when a flocculent precipitate (D) is obtained. Table II gives a schematic representation of the various treatments given to the material for isolating the different fractions.

The nitrogen and phosphorus contents of the five fractions in percentages of the material as also their N : P ratios are given in Table III. C_1 represents the ether soluble portion and represents the cadmium compound

TABLE III

		A	B	C_1	C_2	D
Nitrogen	..	+	0.75	0.58	0.96	1.08
Phosphorus	..	+	0.78	1.32	0.68	0.06
N : P	2.5 : 1	1 : 1	3 : 1	..

of the true lecithin, a striking confirmation of which is obtained by the analytical data presented in Table III. B corresponds in composition to sphingomyelin. Fraction D contains nitrogen, is strongly hygroscopic, and freely soluble in water from which it can be reprecipitated by the addition of 10 volumes of absolute alcohol or acetone. The product has a very low content of phosphorus which can be eliminated by further purification. All attempts at obtaining crystalline substances from the crude product have so far been unsuccessful. The crude product is optically active, contains sulphur and on hydrolysis with dilute acids readily splits off a reducing sugar which has been identified as galactose both by its osazone and mucic acid tests.

A further fractionation of the crude galactolipins was carried out by dissolving the product in pyridine in which it was only partially soluble. The pyridine insoluble fraction was kept separate and the pyridine soluble portion was fractionally precipitated by successive additions of chloroform, yielding four fractions, *a*, *b*, *c*, *d*. These were purified by dissolving in dilute alcohol and precipitating with anhydrous acetone. An analysis of these fractions as also those of the crude product and the pyridine insoluble fraction is presented in Table IV.

The analytical data of the above four fractions, *a*, *b*, *c* and *d*, point to the conclusion that the pyridine soluble fraction consists mainly of two

TABLE IV.

		Crude product D	Pyridine insoluble fraction	Pyridine soluble			
				<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
$[\alpha]_D^{25^\circ\text{C}}$	original product ..	31.58	91.22	67.1	28.73	—17.56	—22.22
„	after acid hydrolysis ..	21.05	28.01	22.0	10.85	—2.42	0.00
Nitrogen, N	..	1.08	1.67	1.38	0.34	0.15	0.26
Phosphorus, P	..	0.06	0.21	0.07	0.03	0.01	0.01
Sulphur, S	..	0.12	0.26
Galactose	..	32.89	38.42	43.01	37.55	26.33	31.14

substances, a dextro component predominant in fraction *a*, and a lævo component comprising the fraction *d*. Emulsin acts on both *a* and *d*, indicating thereby that the fractions contain glycosides.

The pyridine insoluble fraction is interesting because of its sulphur content and is being subjected to further investigation.

Summary

1. A preliminary study of the lipins of Fenugreek seeds has been made. Methods for the isolation and fractionation of the lipins are described in detail.

2. A phospholipin allied to sphingomyelin, an oil soluble true lecithin which forms a complex with cadmium salts, a pyridine soluble galactolipin and a galactoside and a pyridine insoluble galactolipin containing sulphur are among the most interesting fractions that have been isolated from the seeds.

3. A detailed investigation of the cadmium complex and the pyridine insoluble galactolipin is under progress.

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ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

Part IV. Halogen Compounds.

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(Communicated by Sir C. V Raman, Kt, F R S., N.L.)

1. Introduction.

PART I of this series contained determinations of ultrasonic velocity in a number of halogen compounds, mainly of the aliphatic class. Therein it was observed, that in general, introduction of one or more heavy atoms such as bromine, tended to bring down the velocity in the compound. The lowest recorded was that for carbon tetrachloride, being 928 metres per second at 23° C

It was thought worthwhile to make such determinations for some more halogen compounds and investigate the influence of substitution on sound velocity.

In Parts I, II and III, the frequency of vibration was taken as that set up initially, the apparatus not being disturbed as one liquid was substituted for another. The experimental arrangement was identical for every liquid studied; and the quartz crystal was just suspended on top of the liquid. Whereas, in this series, it was found necessary at times to tune up the circuit and to determine for every liquid the frequency of oscillation. This was done by means of a Precision wave-meter. Though there was not much difference in the frequency for identical conditions of experimentation, from one liquid to another, it should be emphasised that this method eliminated any possible uncertainty in the frequency.

2. Results

The following table gives determinations of ultrasonic velocity in several halogen compounds. The last column gives the values for adiabatic compressibility for these compounds as calculated from their sound velocities and from separate determinations carried out of their densities as well.

The frequency of oscillation employed was about 7.32×10^6 c./s.

TABLE I

Ultrasonic Velocities in Halogen Compounds at about 7.32×10^6 c./s.

	Liquids	Chemical Formula	Temp. in °C.	Density	Velocity of sound in metres per second	Adiabatic compressi- bility $\beta_\phi \times 10^9$
1	Ethyl bromide ..	C_2H_5Br	28°	1.428	892	88.1
2	Butyl bromide (<i>n</i>) ..	$CH_3(CH_2)_2CH_2Br$	25°·5	1.272	1016	76.2
3	Butyl iodide (<i>n</i>) ..	$CH_3(CH_2)_2CH_2I$	28°	1.616	959	67.3
4	Allyl chloride ..	$CH_2 : CHCH_2Cl$	28°	0.937	1088	90.1
5	Acetylene dichloride (<i>cis</i>) ..	$CHCl \cdot CHCl$	25°·5	1.262	1025	75.4
6	Acetylene tetrachloride ..	$CHCl_2CHCl_2$	28°	1.578	1155	48.6
7	Acetylene tetrabromide ..	$CHBr_2CHBr_2$	28°	2.962	1007	33.3
8	Tetrachlorethylene ..	C_2Cl_4	28°	1.623	1027	58.4
9	Dichlorobenzene- <i>o</i> ..	$C_6H_4Cl_2$	28°	1.294	1246	49.7
10	Dichlorobenzene- <i>m</i> ..	„	28°	1.285	1232	51.2
11	Benzoyl chloride ..	C_6H_5COCl	28°	1.211	1318	47.5
12	Benzyl chloride ..	$C_6H_5CH_2Cl$	28°	1.102	1377	47.8
13	Chlorobenzene ..	C_6H_5Cl	23°	1.101	1302	53.6
14	Bromobenzene ..	C_6H_5Br	28°	1.495	1134	52.0
15	α -Monochloronaphthalene	$C_{10}H_7Cl$	27°	1.189	1462	39.3

3. Discussion.

No data on acoustic velocity are available for the compounds studied in this paper

We observed in earlier papers that acoustic velocities were lowered generally by the introduction of a heavier atom in place of a lighter one. As examples, we quote chloroform and bromoform, methylene halides and ethylene halides. The results of this paper in addition to confirming the view above mentioned, bear out also the effect of double bonds on the velocity. We shall now elaborate our points.

Ethyl and butyl bromides—These bromides show low acoustic velocities compared with other ethyl and butyl compounds. The higher velocity in butyl bromide, as between these two, is due to the greater length of the molecule; and such an effect due to the length of the chain has been noticed

before. Compared with their corresponding alcohols (Part I), the bromides have decidedly lower velocities, due to the introduction of a heavy atom of bromine, in place of .OH.

Ethyl bromide has a velocity of 892 metres/second at 28°C., the lowest so far known in liquids

Butyl halides.—For the same length of the molecule, but with a heavier atom, such as iodine, the acoustic velocity is lowered. This is exemplified in butyl iodide which shows lower velocity than butyl bromide. The adiabatic compressibility for the former compound is smaller than that for butyl bromide.

Acetylene chlorides.—The sound velocities in acetylene dichloride and acetylene tetrachloride have been determined. We should ordinarily expect the tetrachloride to possess lower velocity, as it contains two more chlorine atoms. But surprisingly enough, the dichloride gives 1025 m/s. at 25°.5 C. and the tetrachloride 1155 m/s. at 28° C. This is in spite of the lower density of the dichloride. This can be explained only by the fact that the dichloride is unsaturated, having a double bond, while the tetrachloride is fully saturated. We should presume, therefore, that unsaturation favours lowering of sound velocity; and other such instances will be quoted elsewhere.

Here may be compared the velocity in ethylene chloride $C_2H_4Cl_2$ —a saturated compound—, which is 1240 m/s. at 23° C

Acetylene tetrahalides—The velocity in tetrabromide of acetylene is less than that in the tetrachloride by about 150 metres at 28° C. The observation holds good here, of heavy atom lowering the velocity. The adiabatic compressibility for the tetrabromide is less than that of the tetrachloride

Allyl chloride.—Such a low velocity as was observed for this compound, is due to the presence of both a double bond and a chlorine atom.

Tetrachlorethylene.—That the presence of a double bond favours lower velocity is here again confirmed. Acetylene tetrachloride contains the same number of chlorine and carbon atoms (though 2 more hydrogen atoms) as tetrachlorethylene, but the sound velocity is more by 100 metres at 28° C. This is due to the adiabatic compressibility for C_2Cl_4 being greater. The only possible explanation seems to be that the double bond, present in C_2Cl_4 , is responsible for these effects.

Dichlorobenzenes.—We observed earlier that in general, the ortho-substituted compound shows slightly higher acoustic velocity. This is also the case with the dichlorobenzenes, the ortho-dichlorobenzene having higher sound velocity.

Comparison can be made of the velocity in chlorobenzene, which contains only one chlorine atom. The velocity in it was found to be 1302 m./s. at 23° C. and making allowance for diminution in it for higher temperature (28° C.), the velocity is still higher than those for the dichlorobenzenes. A greater number of heavier atoms in the molecule decreases the velocity.

Bromobenzene —The velocity in this compound is only 1134 metres/second at 28° C., which is very low for an aromatic liquid. This is much lower than that for chlorobenzene, as is to be expected on the introduction of a heavy atom. The density for bromobenzene is much higher than that for chlorobenzene, while the adiabatic compressibility is only slightly less.

It may be remarked here that bromobenzene has a velocity much lower than that for any of the dichlorobenzenes, by nearly 100 metres at 28° C. But the adiabatic compressibilities for these compounds are about the same.

Benzyl and Benzoyl chlorides —Benzyl chloride has a velocity of 1377 metres/second while the other has 1318 metres/second both at 28° C. The higher velocity in the former compound is explained by the fact that it possesses lower density, with a compressibility nearly equal to that of the latter compound.

α -Monochloronaphthalene —This compound gives an acoustic velocity of 1462 m./s. at 27° C. Freyer, Hubbard and Andrews,² in their paper, have determined in the analogous bromine compound the sound velocity and they give it for 414 kc., as 1350 m./s. at 27° C. This is definitely lower than that for the chlorine compound and what has been so often said regarding the substitution of a heavy atom, here again finds confirmation.

It is a pleasure to thank Sir C. V. Raman, Kt., F.R.S., N.L., for his interest in the work.

4 Summary

The paper gives ultrasonic velocities at about 7.32×10^6 c./s., and adiabatic compressibilities calculated therefrom, in 15 halogen substituted compounds, of both aliphatic and aromatic series. It is found in general, from a consideration of the results, that (1) introduction of a heavier atom lowers acoustic velocity, and (2) the presence of a double bond—or unsaturation—favours lowering of the velocity.

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UPON SOME NEW RESULTS IN THE DOMAIN OF NON-LINEAR MECHANICS.

BY PROF. DR. N. KRYLOFF

AND

PROF. DR. N. BOGOLIUBOFF, KIEFF, URSS.

Received May 5, 1936.

[Extract from a letter to Prof D. D. Kosambi.]

ALTHOUGH our methods could be applied to the general case $\phi = \phi(x, y, t)$ (provided ϕ is relatively small with respect to n), we shall treat in what follows only the case when $\phi = p \sin qt$, the value of p being sufficiently small as compared with n

We shall obtain for this case the first approximation. The relative error in periods will be of the order of magnitude of $\left(\frac{p}{n}\right)^2$.

In the equations

$$(1) \quad \frac{d^2x}{dt^2} + n^2x = p \sin qt \frac{dy}{dt}; \quad \frac{d^2y}{dt^2} + n^2y = -p \sin qt \frac{dx}{dt}$$

we shall suppose first that n is sufficiently near to $\frac{r}{s} q$, r and s being some mutually prime integers

Let us change the variables (compare to the well-known method "de la variation des constantes arbitraires").

$$(2) \quad \begin{cases} x = a \sin \frac{r}{s} qt + b \cos \frac{r}{s} qt; \\ \frac{dx}{dt} = a \frac{r}{s} q \cos \frac{r}{s} qt - b \frac{r}{s} q \sin \frac{r}{s} qt; \\ y = \alpha \sin \frac{r}{s} qt + \beta \cos \frac{r}{s} qt; \\ \frac{dy}{dt} = \alpha \frac{r}{s} q \cos \frac{r}{s} qt - \beta \frac{r}{s} q \sin \frac{r}{s} q; \end{cases}$$

where a, b, α, β are new unknown functions of t .

By substituting these expressions in (I) we obtain after some evident computations the following system of equations equivalent to the primary system (I).

$$(3) \left\{ \begin{aligned} \frac{r}{s} q \frac{da}{dt} &= \left[p \sin qt \left\{ a \frac{r}{s} q \cos \frac{r}{s} qt - \beta \frac{r}{s} q \sin \frac{r}{s} qt \right\} \right. \\ &\quad \left. + \left\{ \left(\frac{r}{s} q \right)^2 - n^2 \right\} \left\{ a \sin \frac{r}{s} qt + b \cos \frac{r}{s} qt \right\} \right] \cos \frac{r}{s} qt; \\ \frac{r}{s} q \frac{db}{dt} &= - \left[p \sin qt \left\{ a \frac{r}{s} q \cos \frac{r}{s} qt - \beta \frac{r}{s} q \sin \frac{r}{s} qt \right\} \right. \\ &\quad \left. + \left\{ \left(\frac{r}{s} qt \right)^2 - r^2 \right\} \left\{ a \sin \frac{r}{s} qt + b \cos \frac{r}{s} qt \right\} \right] \sin \frac{r}{s} qt; \\ \frac{r}{s} \frac{da}{dt} &= \left[- p \sin qt \left\{ a \frac{r}{s} q \cos \frac{r}{s} qt - b \frac{r}{s} q \sin \frac{r}{s} qt \right\} \right. \\ &\quad \left. + \left\{ \left(\frac{r}{s} q \right)^2 - n^2 \right\} \left\{ a \sin \frac{r}{s} qt + \beta \cos \frac{r}{s} qt \right\} \right] \cos \frac{r}{s} qt; \\ \frac{r}{s} \frac{d\beta}{dt} &= - \left[- p \sin qt \left\{ a \frac{r}{s} q \cos \frac{r}{s} qt - b \frac{r}{s} q \sin \frac{r}{s} qt \right\} \right. \\ &\quad \left. + \left\{ \left(\frac{r}{s} q \right)^2 - n^2 \right\} \left\{ a \sin \frac{r}{s} qt + \beta \cos \frac{r}{s} qt \right\} \right] \sin \frac{r}{s} qt. \end{aligned} \right.$$

We see at once that these equations are of the form

$$\frac{dx_k}{dt} = X_k(x_1, \dots, x_n; t), \quad k = 1, 2, \dots, n,$$

where the right-hand parts are sufficiently small and periodic (with a period $\tau = \frac{2\pi s}{q}$) with respect to t

In order to obtain the first approximation of the system of such a kind we have established a principle, which we have called—the *Averaging Principle*.

According to this Principle for the obtaining of the first approximation we may average the right-hand members of (4) with respect to t (during this averaging x_1, x_2, \dots, x_n must be considered as constants) Hence instead of (4) we obtain the following equations of the first approximation :

$$\frac{dx_k}{dt} = \frac{1}{\tau} \int_0^\tau X_k(x_1, x_2, \dots, x_n, t) dt, \quad k = 1, 2, \dots, n.$$

By applying this tool to the system (3) we get in the case when $\frac{r}{s} \neq \frac{1}{2}$ (that is if n is not near to $\frac{q}{2}$):

$$\begin{aligned} 2 \frac{r}{s} q \frac{da}{dt} &= \left[\left(\frac{r}{s} q \right)^2 - n^2 \right] b; & 2 \frac{r}{s} q \frac{db}{dt} &= - \left[\left(\frac{r}{s} q \right)^2 - n^2 \right] a; \\ 2 \frac{r}{s} q \frac{da}{dt} &= \left[\left(\frac{r}{s} q \right)^2 - n^2 \right] \beta; & 2 \frac{r}{s} q \frac{d\beta}{dt} &= - \left[\left(\frac{r}{s} q \right)^2 - n^2 \right] \alpha. \end{aligned}$$

But neglecting the square $\left[n - \frac{r}{s} q\right]^2$ we have

$$\left(\frac{r}{s} q\right)^2 - n^2 = \left(\frac{r}{s} q\right)^2 - \left[\frac{r}{s} q + \left(n - \frac{r}{s} q\right)\right]^2 \simeq 2 \frac{r}{s} q \left(\frac{r}{s} q - n\right)$$

and therefore we obtain approximately

$$a = A \sin \left[\left(\frac{r}{s} q - n\right) t + \psi \right]; \quad b = A \cos \left[\left(\frac{r}{s} q - n\right) t + \psi \right];$$

$$\alpha = B \sin \left[\left(\frac{r}{s} q - n\right) t + \theta \right]; \quad \beta = B \cos \left[\left(\frac{r}{s} q - n\right) t + \theta \right];$$

where A, B, ψ, θ are the constants of integration.

We thus have

$$x = A \cos (nt + \psi); \quad y = B \cos (nt + \theta)$$

and we see also that in the case where n is not near to $\frac{q}{2}$ (case of the non-resonance) the first approximation gives for the period the value $\frac{2\pi}{n}$.

The corrections to this value being thus of the order of smallness of $\left(\frac{p}{n}\right)^2$ further approximations must be calculated in order to get an idea of the influence of p, q on the value of the period. These further approximations for some analogous cases were detailed in our book *Les méthodes de la Mécanique non linéaire appliquées à la théorie des oscillations stationnaires* (Kieff, 1934).

Let us now return to the case where $\frac{r}{s} = \frac{1}{2}$, that is where $n \sim \frac{q}{2}$ (case of resonance). For this case the equations of the first approximation are :

$$q \frac{da}{dt} = \left[\left(\frac{1}{2} q\right)^2 - n^2\right] b - \frac{\beta p q}{4};$$

$$q \frac{db}{dt} = - \left[\left(\frac{1}{2} q\right)^2 - n^2\right] a - \frac{\alpha p q}{4};$$

$$q \frac{d\alpha}{dt} = \left[\left(\frac{1}{2} q\right)^2 - n^2\right] \beta + \frac{b p q}{4};$$

$$q \frac{d\beta}{dt} = - \left[\left(\frac{1}{2} q\right)^2 - n^2\right] \alpha + \frac{a p q}{4};$$

where we may also put

$$\left(\frac{1}{2} q\right)^2 - n^2 \simeq q \left(\frac{q}{2} - n\right).$$

The above system is a linear system with constant coefficients and its characteristic equation will be

$$\left(\lambda^2 + \delta^2 + \frac{p^2}{4}\right) = 0, \quad \text{where, } \delta = \frac{q}{2} - n.$$

Hence

$$\lambda = \pm j \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

The frequencies of a , b , α , β will be therefore

$$\pm \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

and thence we obtain the frequencies of (x, y)

$$\frac{q}{2} \pm \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}$$

We also see that in this case, when n is near to $\frac{q}{2}$ (resonance of de-multiplication) the first order approximation of period is not equal simply to $\frac{2\pi}{n}$, as in the previous case, but :

$$\frac{2\pi}{\frac{q}{2} \pm \sqrt{\left(\frac{q}{2} - n\right)^2 + \left(\frac{p}{2}\right)^2}}$$

In this letter we have made only a brief sketch of the application of our methods to your very interesting problem.

A more detailed study with suitable demonstrations may constitute a subject of an extensive paper which we hope to write in the near future.

THE RAMAN SPECTRA OF PROPYLENE AND ISO-BUTANE.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1 Introduction.

A CAREFUL and systematic study of the Raman spectra of the more simple organic and inorganic molecules, comprising the intensity and polarisation characters of the modified lines is obviously of great importance from the standpoint of their chemical constitution. Investigations in this direction have been taken up by Cabannes and Rousset, Lenard Simons, Langseth, Trumpy and others, who have shown that the polarisation characters of the Raman lines in certain simple molecular types when interpreted in the light of Placzek's theory are in good agreement with the accepted chemical constitution, and enable definite decisions to be made in cases where the structure is uncertain or controversial. The present communication describes the results of the study of the Raman spectra of propylene and iso-butane.

2 Experimental.

The gases were taken directly from commercial cylinders supplied by the Ohio Chemical and Manufacturing Co., Ltd. Propylene was labelled 99.5% pure, while the guaranteed degree of purity in the case of iso-butane was 99%. The gases were condensed in thick-walled pyrex glass tubes cooled in a bath of alcohol and carbon-dioxide snow, after being dried and rendered dust-free by passing successively over anhydrous P_2O_5 and a long plug of compressed cotton wool. The tubes were sealed off leaving sufficient space for the expansion of the liquids. The spectra were taken at the room temperature using a Hilger two-prism spectrograph of high light gathering power. A quartz mercury arc served as the source of illumination and was focussed on the Raman tube by a large glass condenser. The time of exposure to get an intense picture was about 50 hours using a slit width of .05 mm. In order to determine the state of polarisation of the Raman lines a quartz double image prism with its axes horizontal and vertical was interposed between the slit of the spectrograph and the observation end of the Raman tube, and the horizontal and vertical components of the scattered radiation were photographed separately and simultaneously in the usual manner.

3. Results.

In what follows, the polarisation characters of the various Raman lines are indicated by the letters P and D, the letters having the following significance :

$$P \leq \frac{6}{7} \quad : \quad D \approx \frac{6}{7}$$

The quantitative estimates of depolarisation require correction under two heads : (1) convergence of the incident light beam which tends to enhance the genuine depolarisation¹, (2) unequal losses of the two components of the scattered radiation by reflection at the prism faces whereby the vertical component loses more than the horizontal, thus producing an apparent increase in the depolarisation

(1) *Propylene*—Next to ethylene, propylene forms the simplest member of the olefine series of hydrocarbons, having the general formula C_nH_{2n} . However, although investigations in the cases of ethylene are quite numerous, the Raman spectrum of propylene does not appear to have been completely analysed.† Table I gives the complete analysis of the Raman spectrum of this substance in the region between λ 4046 and λ 5100 :

TABLE I.
Raman Spectrum of Propylene $H_2C=CHCH_3$

No.	ν	Assignment	Int.	Poln.	No.	ν	Assignment	Int.	Poln.
1	19930	<i>e</i> —3008	2 <i>b</i>	P	22	21974	<i>k</i> —2731	1	P
2	19948	<i>e</i> —2990	0		23	22018	<i>e</i> — 920	6	P
3	20014	<i>e</i> —2921	4	P	24	22358	{ <i>e</i> — 580	$\frac{1}{2}$ <i>d</i>	D
4	20052	<i>e</i> —2886	$\frac{1}{2}$	P			{ (band)		
5	20082	<i>e</i> —2856	$\frac{1}{2}$		25	22506	<i>e</i> — 432	4	P
6	20204	<i>e</i> —2734	0	P	26	23058	<i>k</i> —1647	8	P
7	21289	<i>e</i> —1649	10 <i>s</i>	P	27	23295	<i>k</i> —1410*	4	P
8	21511	<i>i</i> —3010	0 <i>d</i>		28	23368	<i>e</i> — 430	0	P
9	21518	<i>e</i> —1420*	5	P	29	23407	<i>k</i> —1298*	8	P
10	21595	<i>i</i> —2921	$\frac{1}{2}$	P	30	23785	<i>k</i> — 920	5	P
11	21618	<i>k</i> —3087	$\frac{1}{2}$		31	24273	<i>k</i> — 432	2	P
12	21642	<i>e</i> —1296*	8	P	32	24286	<i>o</i> —3013	0	
13	21694	<i>k</i> —3011	6 <i>b</i>	P	33	24298	{ <i>q</i> —3090	$\frac{1}{2}$ <i>d</i>	P
14	21719	<i>k</i> —2896	1	P			{ <i>o</i> —2995		
15	21749	<i>k</i> —2956	0		34	24372	{ <i>q</i> —3016	2	P
16	21781	<i>k</i> —2924	10	P			{ <i>o</i> —2921		
17	21812	<i>k</i> —2893	4	P	35	24392	<i>q</i> —2996	$\frac{1}{2}$	P
18	21847	<i>k</i> —2858	1	P	36	24406	<i>o</i> —2887	1	P
19	21882	<i>k</i> —2823	$\frac{1}{2}$	P	37	24429	<i>p</i> —2924	2	P
20	21910	<i>k</i> —2795	0		38	24462	<i>q</i> —2926	4	P
21	21942	<i>k</i> —2763 †	00						

¹ R. Ananthakrishnan, *Proc. Ind. Acad. Sci., A*, 1935, 2, 133

† The Raman Spectrum of propylene has been studied by M. Bourguet (*C.R.*, 1932, 194, 1736) who has reported the following frequencies.—

$\Delta\nu(\text{cm.}^{-1})$.. 1295 1414 1647 3007 3086
Int. .. 6 3 6r 3br 4*Bd*

$\Delta\nu(\text{cm.}^{-1})$..	432	580	920	1297*	1415*	1648	2732	2763	2795	2823	2857	
Int.	..	3	$\frac{1}{2}bd$	6	8	4	10s	1	00	0	$\frac{1}{2}$	1
ρ	..	P	D	P	P	P	P	P		P	P	
$\Delta\nu(\text{cm.}^{-1})$..	2890	2924	2956	2990	3010	3087						
Int.	..	4	10	0	1	6b	$\frac{1}{2}$					
ρ	..	P	P		P	P						

(2) *Iso-Butane*.—The Raman spectrum of iso-butane in the liquid state has been studied by Bhagavantam² and later by Kohlrausch and Köppl³ with practically identical results. As will be seen from Table II, the author's results stand in good agreement with those of the above workers. The state of polarisation of the Raman lines is given in the last column.

TABLE II.

Raman Spectrum of Iso-Butane H.C (CH₃)₃.

Bhagavantam	Kohlrausch & Köppl	Author		
		$\Delta\nu(\text{cm.}^{-1})$	Int.	ρ
372 (4b)	370 (4b)	370	4b	D
436 (2b)	438 (1)	437	1	P
796 (10)	794 (9)	795	10	P
967 (5b)	962 (4b)	965	4b	D
	1098 ($\frac{1}{2}b$)			
1177 (5b)	1168 (4sb)	1170	4b	D
1355 (4b)	1322 (3b)	1325	3b	D
1453 (10b)	1452 (7b)	1452	7b	D
2624 (1)	2628 (0)	2625	$\frac{1}{2}$	P
2720 (4)	2718 (7b)	2720	4	P
2777 (2)	2778 (2)	2780	2	P
2870 (10)	2868 (14b)	2870*	15	P
2892 (2)		2890	2	
2910 (3)	2906 (7)	2908	5	P
2936 (3)	2936 (4)	2935	5	P
2962 (8)	2959 (12)	2960*	10	D (?)

4 Discussion of Results.

(1) *Propylene* H₂C : CH.CH₃ —As might be expected from the high value of the depolarisation for the gas,⁴ the Raman spectrum of liquid propylene shows an intense wing accompanying the unmodified Rayleigh lines.

² S. Bhagavantam, *Ind Jour Phys.*, 1931, **6**, 695.

³ K. W. F. Kohlrausch and F. Köppl, *Z. f. Phys. Chem.*, 1934, **26**, 209.

⁴ R. Ananthakrishnan, *Proc. Ind. Acad. Sci., A*, 1935, **2**, 156.

However, no minimum of intensity is perceptible for the wing in the close vicinity of the Rayleigh line. The characteristic feature of the Raman spectrum of propylene is that almost all the Raman lines are quite sharp, and more or less well polarised. The intense and well-polarised Raman line at 1648 cm^{-1} represents the $\text{C}=\text{C}$ oscillation, while the polarised Raman frequency at 920 cm^{-1} presumably arises from the $\text{C}-\text{C}$ oscillation. The frequency at 432 cm^{-1} is much less polarised than the first two and is in all probability the transverse frequency of the carbon chain. These three frequencies represent thus the fundamental frequencies of the carbon atoms.

The Raman lines at 1297 cm^{-1} and 1410 cm^{-1} are to be attributed to $(\text{C}-\text{H})$ deformation vibrations. It is noteworthy, that unlike the broad and depolarised $(\text{C}-\text{H})$ δ frequency in the case of the saturated aliphatic hydrocarbons, these two lines are sharp and depolarised to an extent less than $6/7$. The polarisation photograph clearly shows that while the vertical component is quite sharp, the horizontal components of these two frequencies are rather diffuse.

The large number of frequencies in the 3.5μ region have their origin in the oscillations of the hydrogen atoms, and their intensities are distributed over a wide range. A depolarised Raman band extends in the interval between $\Delta\nu = 2924\text{ cm}^{-1}$ and $\Delta\nu = 3010\text{ cm}^{-1}$.

(2) *Iso-Butane* $\text{H C}(\text{CH}_3)_3$ —A striking contrast is noticed when one compares the Raman spectra of propylene and iso-butane. Most of the lines in the latter spectrum are broad and many of them are badly polarised in contrast to the sharp and well-polarised lines of the former. This difference is perhaps due to the symmetry of the iso-butane molecule which causes many of the vibrations to be degenerate. The wings accompanying the Rayleigh line in the Raman spectrum of iso-butane are much less prominent than in the case of propylene in conformity with the low depolarisation of the vapour.⁵

The molecule of iso-butane can be designated by ZXY_3 , Z and X being on the symmetry axis. The model has the symmetry C_{3v} , (analogous for instance to the molecule H C Cl_3) and possesses three totally symmetrical and three doubly degenerate vibrations, all the six being allowed in the Raman effect as well as in the infra-red. The normal vibrations of the model have been diagrammatically represented and discussed in some detail by Kohlrausch.⁶ The following figures are reproduced from his paper.

⁵ R. Ananthakrishnan, *loc. cit.*

⁶ K. W. F. Kohlrausch, *Z. f. Phys. Chem.*, B, 1935, 28, 340.

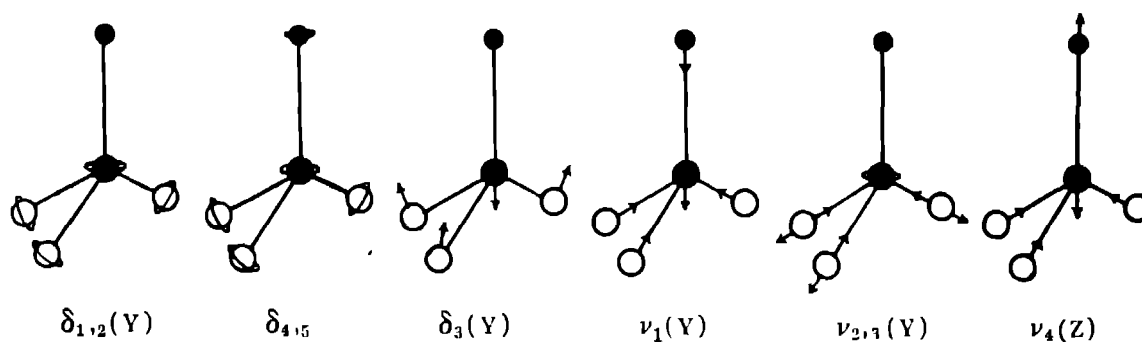


FIG. 1. Normal Vibrations of the ZXY_4 molecule

The polarisation photograph of iso-butane shows at a glance that Kohlrausch's classification of the iso-butane frequencies requires revision. He gives the following classification :

$$\begin{array}{lcl}
 \omega_1 = \nu_1(\text{CH}_3) = 795 \text{ cm.}^{-1} & & \\
 \omega_2 = \delta_3(\text{CH}_3) = 370 \text{ ,,} & \left. \vphantom{\begin{array}{l} \omega_1 \\ \omega_2 \end{array}} \right\} & \text{totally symmetric vibrations} \\
 \nu_4(\text{H}) \approx 3000 \text{ ,,} & & \\
 \omega_3 = \nu_{2,3}(\text{CH}_3) = 965 \text{ ,,} & & \\
 \omega_4 = \delta_{1,2}(\text{CH}_3) = 437 \text{ ,,} & \left. \vphantom{\begin{array}{l} \omega_3 \\ \omega_4 \end{array}} \right\} & \text{doubly degenerate vibrations} \\
 \delta_{4,5} > 1000 \text{ ,,} & &
 \end{array}$$

The Raman line at 437 cm^{-1} is well polarised, and hence cannot be the doubly degenerate frequency $\delta_{1,2}$. On the other hand, $\Delta\nu = 370 \text{ cm}^{-1}$ is highly depolarised and is presumably degenerate. These two frequencies have therefore to be interchanged in the above classification

The Raman lines at 1170, 1325 and 1452 cm^{-1} are all depolarised to the limiting value $6/7$. From the fact that it occurs practically in all the saturated aliphatic hydrocarbons, we conclude that the depolarised line at 1452 cm^{-1} arises from the (C—H) δ vibration of the CH_3 group. Which of the two frequencies 1170 and 1325 is to be associated with $\delta_{4,5}$ is not clear from the polarisation measurements

In the region of higher frequencies, there are no less than eight lines, showing a wide range of intensities. The polarisation photograph shows a remarkable feature in the case of the two intense lines at 2870 and 2960. In both cases, the vertical component is quite sharp, while the horizontal component is broad and diffuse. Presumably, there is a superposition of a polarised Raman line and a depolarised Raman band in these two cases. In the host of hydrogen frequencies, the identification of $\nu_4(\text{H})$ is a matter of some difficulty. The following table gives a comparison of the Raman spectra of H.C.Cl_3 and $\text{H.C.}(\text{CH}_3)_3$.—

TABLE III.

H.C.Cl_3	$\Delta \nu$	259	364	664	756	1214	3016
	ρ^{\dagger}	.87	.19	.07	.86	.87	.20
$\text{H.C.}(\text{CH}_3)_3$	$\Delta \nu$	370	437	795	965	1325	?
	ρ	D	P	P	D	D	

Only the pertinent frequencies of iso-butane are included in the table. The similarity of the two spectra is strikingly brought out by the polarisation results.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest and encouragement in the course of the present work

5. Summary.

The Raman spectrum of propylene has been reported in detail and the observed frequencies are discussed in the light of the knowledge of their state of polarisation. The frequencies 1648, 920 and 432 are identified as the fundamental frequencies of the carbon chain, the first two being of the valence type, while the third one represents a deformation frequency. The fourteen additional lines are to be attributed to the oscillations of the hydrogen atoms. The Raman lines of propylene are characterised by extreme sharpness, and are more or less well polarised. The Raman spectrum of iso-butane forms a striking contrast, many of the lines being extremely broad and highly depolarised. It is suggested that this difference might be due to the symmetry of the iso-butane molecule which causes many of the vibrations to be degenerate. An attempt has been made to interpret the spectrum of iso-butane with the help of the polarisation data. The close similarity between the Raman spectra of iso-butane and chloroform as revealed by polarisation studies is pointed out.

[†] L. Simons, *Comm. Phys.-Math. Soc. Scient. Fenn.*, 1932, 6, 13.

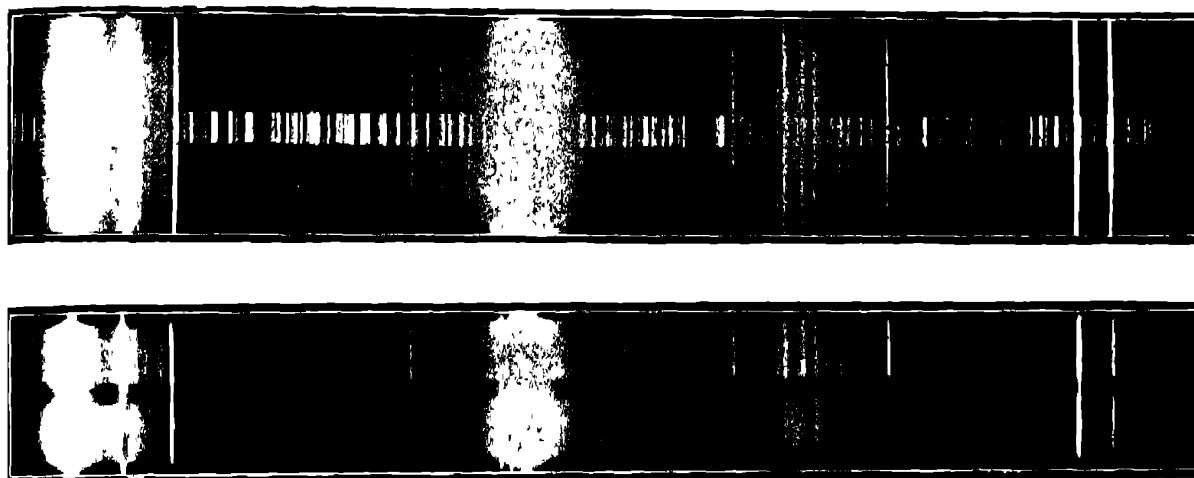


FIG 2. Raman Spectrum of Propylene

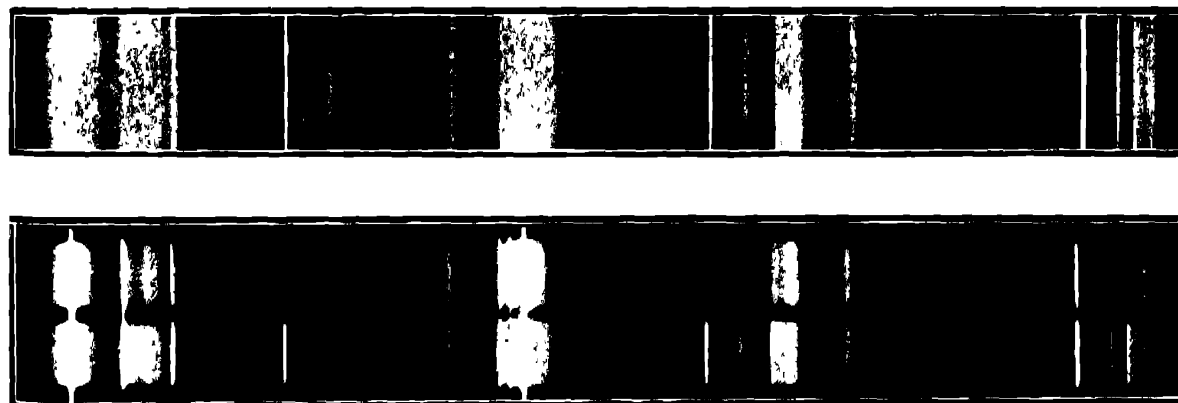


FIG 3. Raman Spectrum of Iso Butane

THE RAMAN SPECTRA OF SELENIOUS ACID AND ITS SODIUM SALTS.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

RECENTLY in a note to *Current Science*¹ the author published the preliminary results of an investigation on the Raman spectrum of crystalline selenious acid. Then it was pointed out that the spectrum of the solid consists of not less than twelve sharp lines and is essentially different from that of its aqueous solution which has been reported on by Pringsheim and Yost.² To understand fully the significance of these lines in the solid, a detailed study of the problem has been undertaken and this report presents the results obtained both with the acid in the solid and molten states and in aqueous and alcoholic solutions and with the selenite and biselenite of sodium.

2. Experimental Method and Results.

The experimental procedure was the same as has been described in the previous communications to these *Proceedings*. The substance used in this investigation was the anhydrous acid supplied by Kahlbaum. Fresh selenious acid prepared by the oxidation of selenium with concentrated nitric acid and purified by repeated recrystallisations from water gave an identical spectrum. The anhydrous acid shows a marked tendency to decompose on heating but the hydrated variety melts at about 70° C to a light yellow liquid. For all purposes, this liquid is to be considered only as a solution of H_2SeO_3 in its water of crystallisation. It gave an intense spectrum with the 4358 radiations of the mercury arc; but the 4047 line of the source was partially absorbed. The separation of amorphous selenium due to the action of light on the acid in the aqueous and alcoholic solutions gave rise to increased Tyndall scattering; yet tolerably good pictures were obtained by carefully filtering the solutions several times through thick folds of filter paper.

¹ Venkateswaran, C. S., *Current Science*, 1935, 4, 309.

² Pringsheim and Yost, *Z. Physik*, 1929, 58, 1.

The biselenite of sodium was prepared by titrating with a solution of sodium hydroxide using *p*-nitrophenol as indicator and the selenite by using thymolphthalein as indicator.

The spectrograms were measured by means of a Hilger Cross-slide microscope in comparison with an iron arc spectrum. The results are given in Tables I, II and III and the enlarged photographs of some of the spectra are reproduced in the accompanying plate.

TABLE I
H₂SeO₃ Crystal (*d* = 4047, *e* = 4077 and *h* = 4358)

No	Raman lines		$\Delta \nu \text{ cm}^{-1}$	Intensity	Assignment
	wave length	wave-number			
1	4047.0	24581	124	2	<i>d</i>
2	4088.3	24453	252	4	<i>d</i>
3	4094.0	24418	287	2	<i>d</i>
4	4096.0	24407	298	1	<i>d</i>
5	4107.0	24342	363	0	<i>d</i>
6	4120.5	24262	254	2	<i>e</i>
7	4126.1	24229	287	0	<i>e</i>
8	4134.5	24180	528	3br	<i>d</i>
9	4146.8	24108	597	8	<i>d</i>
10	4166.1	23996	709	3	<i>d</i>
11	4179.4	23920	596	3	<i>e</i>
12	4197.3	23818	887	8	<i>d</i>
13	4195.9	23826	888	1	<i>h</i>
14	4201.1	23796	909	2	<i>d</i>
15	4206.9	23761	911	1	<i>d</i>
16	4231.4	23626	890	2	<i>e</i>
17	4246.4	23543	605	2	<i>h</i>
18	4303.9	23228	290	1	<i>h</i>
19	4311.6	23187	249	2	<i>h</i>
20	4321.9	23132	194	1	<i>h</i>
21	4396.5	22739	199	3	<i>h</i>
22	4407.3	22683	255	6	<i>h</i>
23	4415.9	22639	299	2	<i>h</i>
24	4428.7	22574	364	0	<i>h</i>
25	4460.3	22414	524	3	<i>h</i>
26	4475.0	22340	598	8	<i>h</i>
27	4496.6	22234	704	3	<i>h</i>
28	4528.6	22076	862	0	<i>h</i>
29	4534.0	22049	889	10	<i>h</i>
30	4538.2	22029	909	2	<i>h</i>
31	4544.6	21998	940	0	<i>h</i>

R. lines = 124(2), 199(3), 254(6), 287(2), 299(2), 364(0), 524(3), 597(8), 706(3), 862(0), 889(10), 909(2), 940(0).

TABLE II
(Raman Frequencies in cm^{-1}) H_2SeO_3 (Aqueous and Alcoholic Solutions.)

Solid 30° C.	Molten 70° C	Aqueous solutions					Solution in MeOH		Aq. Soln. (Fringsheim and Yost)
		60 %	40 %	30 %	15 %	7.5 %	40 %	15 %	
124(1) 199(3) 254(6) 287(1) 299(2) 364(0) 524(3)	238(1) 343(1) 380(3) 545(1) broad								
597(8)	..	355(2) diff.	355(2)	355(1)	355(1)	..			
706(3)	690(10) ± 30	528(0)	528(0)	528(0)	528(0)	..	589(m) (br)	589(m) (br)	..
862(0)		695
889(10)	892(10) ± 50 (Max. at 862)	695(6) ± 25	695(6) ± 25	695(6) ± 25	695(6) ± 20	695(6) ± 20	
909(2) 940(0)		895(6) ± 30	900(6) ± 25	906(6) ± 20	906(6) ± 15	910(6)	930(m)	935(m)	885

TABLE III.
Raman Frequencies of Sodium Salts Exciting line 4358.3 A.U.

Substance	Raman lines		$\Delta \nu$ in cm^{-1}	Intensity	Previous work
	Wave-length A.U.	Wave-number			
NaHSeO_3 15 % Aq. Solution	4423.0	22603	335	1 (diff.)	339
	4476.0	22335	603	1 (diff.)	..
	4527.5	22076	862	5	853
Na_2SeO_3 10% Aq Solution	4430.8	22563	375	1 (diff)	nil
	4475.0	22340	598	0 (?)	
	4502.5	22204	734	1 (sh)	
	4517.1	22132	806	5	
	4527.5	22076	862	5	

3. Discussion of Results.

The crystalline acid has yielded a spectrum which is very rich in lines, all of which are sharp and well defined. These lines may be divided into five groups, namely, (1) 889 and three companions at 860, 909 and 940, (2) 706, (3) 597 and its companion at 524, (4) 287, 299 and 364 and (5) 124, 199 and 254. Of these lines, the five low frequencies as well as the strong lines 597 and 889 have yielded their antistokes. On melting the solid, all the lines of the first group merge together into one strong broad band with its centre at 892. It is definitely asymmetrical in structure and its maximum intensity is at 862.* The centre of this band shifts to a longer wave-length as the concentration of the solution falls off. Its breadth also gradually diminishes. In the alcoholic solution the shift is distinctly greater than in the aqueous solution of the same concentration by about 30 wave-numbers.

The most remarkable change takes place in the relative intensities of the second and the third group of lines. While in the solid the line at 706 is only of *medium intensity*, in the molten liquid as well as in the aqueous solutions of all concentrations it is the *strongest line* in the spectrum. Its frequency shift is also smaller by about 10 wave-numbers. This line does not at all appear in the alcoholic solutions. On the other hand, the strong line 597 of the solid appears as a faint line at 545 with a finite width in the molten state. The faint satellite 524 of this line is also probably merged into the 545 line of the solution. In the alcoholic solutions, it is the most intense line in the spectrum; but undergoes a distinct lowering of frequency by about 8 wave-numbers.

The fourth group of lines, namely 287, 299 and 364, appear as a doublet with frequency shifts of 343 and 380 in the molten state and a single diffuse band with the centre at 355 in the aqueous solutions. Its presence could not be detected in alcoholic solutions due perhaps to the strong halation following the Rayleigh line.

Of the lines in the fifth group in the solid 124 and 199 completely disappear in the liquid and the solutions, while 254 appears but weakly only in the molten state.

Besides these lines, the water band is present in the aqueous solutions and is prominent when they are dilute. The triple structure of the band is clearly seen and no apparent change in the relative intensities of components is observed. The acid has also practically no influence on the lines of methyl alcohol.

* A study of the polarisation of the acid shows that this line is composed by two different lines and will be reported upon in due course.

4. *Dissociation of Selenious Acid.*

The molecular conductivity of dilute aqueous solutions of Selenious acid^a has been determined by Ostwald who finds that even at a dilution of 1024 litres the conductivity is only about 60% of that of a monobasic acid showing thereby, that it is a very weak acid. He has concluded that it is practically a monobasic acid which assumes the formula $(\text{HO}.\text{SeO}_3).\text{H}$. Therefore, in the aqueous solutions of all concentrations that are investigated by us, we can expect the presence of only the undissociated H_2SeO_3 molecules and HSeO_3' ions formed during the first stage of ionisation.

The Raman spectra of aqueous solutions of concentrations varying from 100% to 7.5% by weight are identical and consist of two prominent lines at about 895 and 695 and a weak, diffuse band at 355. There is sensibly no variation also in the relative intensities of these three lines. These facts point out that the proportion of the molecular species giving rise to them remains practically the same at all concentrations.

Of these three lines, it is significant that the line 895 appears more or less in the same position in the solid, and aqueous and alcoholic solutions. Small changes in the frequency shift of this line depending upon the solvent and the state of dilution are only of an order which could be attributed to the influence of the solvent molecules. For purposes of comparison the frequency shifts of the acid and the salts are collected together in Table IV. The line which corresponds to the symmetrical expansion and contraction of HSeO_3' ion appears at 862 in sodium biselenite.

The proximity of the frequency shift 895 in the acid to the symmetrical line in the biselenite suggests that the former is to be attributed to the HSeO_3' ions in the acid.

On the other hand, the second intense line, 690 in the aqueous solution does not appear in the alcoholic solution, and is rendered weak in the solid; instead, another line is present at about 598 in the latter cases. These two lines presumably belong to two different forms of the undissociated molecule and are discussed fully in a later section.

The spectrum of sodium selenite consists of two lines of medium intensity with frequency shifts of 806 and 862 and two other feeble lines, as is to be expected if we assume a pyramidal model for the SeO_3 radical. The absence of any line at 806 at a concentration of 7.5% clearly indicates that the second stage of ionisation does not begin even at this stage.

^a Landolt and Börnstein Tabellen. 1112.

TABLE IV.

NaHSeO_3	Na_2SeO_3	H_2SeO_3 (molten)	H_2SeO_4 10% Aq.
		238 (1)	
335 (1 dif.)		343 (4)	327 (3 <i>br</i>)
	375 (1)	380 (3)	390 (3 <i>br</i>)
603 (1)	598 (0)	545 (1)	
	734 (1)	690 (10 <i>br</i>)	737 (3 <i>br</i>)
	806 (5)		846 (1)
862 (5)	862 (5)		866 (10)
		892 (10 <i>br</i>)	910 (0)
			929 (1)

TABLE V

NaHSO_3	Na_2SO_3	H_2SO_3	H_2SO_4 (incomplete)
242 (1)			
320 (1)			
420 (1)	471 (1)		521
565 (3)	602 (1)	569	574
826 (1)			
985 (2)	984 (4)		985
1009 (2)		1047	1047
		1142 (<i>str</i>)	
		1199	

The general conclusion, therefore, regarding ionisation of the acid is that the dissociation of $\text{H}_2\text{SeO}_3 \rightarrow \text{H}^\circ + \text{HSeO}_3'$ starts from the solid and the degree of dissociation remains practically constant at the concentrations

employed. In agreement with the conductivity measurements, no further ionisation of HSeO_3' is evident even in dilute solutions.

It has been reported recently that selenic acid⁴ behaves in the Raman effect in the same manner as its analogue, sulphuric acid. But the selenious acid shows marked differences from sulphurous acid. In Table V the Raman frequencies of sulphurous acid and its salts are reproduced from a paper by Fadda.⁵ Unlike selenious acid, there is no common likeness between the spectrum of this acid and those of Sodium sulphite and bisulphite. The lines 569 and 1047 are similar to those attributed to HSO_4' ions in sulphuric acid and are, therefore, due to the oxidation of a part of sulphurous acid to sulphuric acid. As can be seen from Table V there is no such common lines between selenic and selenious acids and hence shows that the latter does not undergo oxidation so easily as sulphurous acid. The presence of the strong line at 1142 in sulphurous acid which is characteristic of SO_2 gas,⁶ confirms that further, most of the gas exists in a state of solution with water and only a small percentage of it is probably present as H_2SO_3 molecules. The line 1199 has been assigned to HSO_3' ions. Thus selenious acid seems to be more stable than its analogue sulphurous acid.

5 Constitution of Selenious Acid

According to chemical evidence, the two possible forms in which selenious acid could exist are the symmetrical form $\text{O} = \text{Se} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$ or the un-

symmetrical form $\begin{matrix} \text{O} & & \text{OH} \\ & \diagdown & / \\ & \text{Se} & \\ & / & \diagdown \\ \text{O} & & \text{H} \end{matrix}$. In the former, selenium is quadrivalent

and both the hydrogen atoms belong to the hydroxyl groups. In the latter, selenium is hexavalent and the acid is the pseudo-acid in which changes in constitution take place to restore it to the first type before any physical or chemical reaction starts with it. From a study of the heat of solution of this acid in different solvents Karve⁷ concludes that it is an associated pseudo-acid in the pure condition and the aqueous solution contains a small percentage of the hydrate of the true acid. However, measurements of conductivity, hydrogen ion concentration, heat of solution and other physico-chemical properties do not always lead to conclusive results⁸ regarding the true nature of the acid.

⁴ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1936, **3**, 307

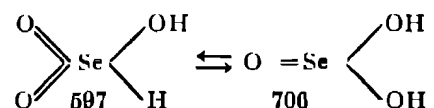
⁵ Fadda, *Nuovo Cimento*, 1932, **9**, 168

⁶ Bhagavantam, S., *Ind. Jour. Phys.*, 1931, **6**, 319

⁷ Karve, D. D., *Jour. Ind. Chem. Soc.*, 1925, **2**, 128

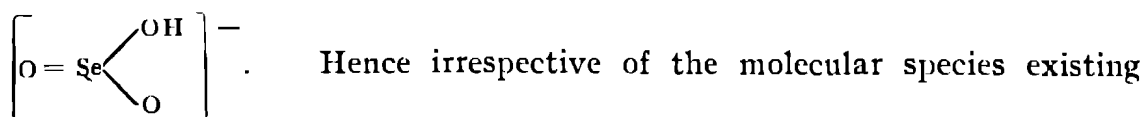
⁸ Stewart, A. W., *Some Physico-Chemical Themes*, Longmans, 1922.

From the point of view of the Raman effect it is evident that the two forms of the acid given above should yield their own lines of entirely different frequencies. As has been pointed out before, one of the striking features in the spectra of the acid in the different states of existence is the remarkable change in the intensity of the two lines 706 and 597 of the solid as it passes to solution in water. These changes in intensity could be easily understood on the postulate that the two forms of the acid are in a state of dynamic equilibrium as follows —



The line with a frequency shift of 597 is characteristic of the unsymmetrical type and 706 of the symmetrical type. The former is more predominant than the latter in the solid and hence the increased intensity of the line 597. The existence of the line 706, in the crystalline acid shows that the latter type is also present in it. As is to be expected, solution of the acid in methyl alcohol contains only the unsymmetrical form and gives the intense line at about 589. In the aqueous solution the reverse process sets in and almost the whole of the acid assumes the symmetrical structure. This contributes to the increased intensity of the line 706. In the molten state when the acid is in solution with its water of crystallisation, a weak line is present at 567 and indicates the persistence of the unsymmetrical form under that condition.

According to the theory of pseudo-acids the first ionisation product of both the types of molecules is identical and the biselenite ion has a structure



in the solid and the aqueous and the alcoholic solutions, a certain percentage of HSeO_3^- ions is formed during the first stage of dissociation and this accounts for the appearance of the line of frequency shift of 895 more or less in the same position in all states.

Thus, the solid or the solutions present a complicated system consisting of two or three molecular species and it is difficult to assign the low frequencies that are observed to any one of them. But in comparison with the Raman spectra of iodic acid⁹ or nitric acid, it may be suggested that the two low frequencies at 343 and 380 in the molten liquid which appear as a single diffuse line at 355 in more dilute solutions

⁹ Venkateswaran, C. S., *Proc. Ind. Acad. Sci., A*, 1935, 2, 119.

belong to the vibrations corresponding to the second parallel vibration of the molecules of the AX_3 type. Of these 343 coincides fairly well with the low frequency at 335 in the sodium biselenite and is due to $HSeO_3'$ ions. The corresponding line of the SeO_3 radical appears at 375 in the sodium selenite solution. The other frequency 380 may, therefore, belong to the symmetrical form of H_2SeO_3 molecules. As has been discussed before, these two frequencies of the solution are replaced by three sharp lines 287, 299 and 364 in the solid. There is one more line at about 524 which is of medium intensity in the solid and which is present weakly in the aqueous solutions of the acid. This line is also to be attributed to one of the normal modes of vibration of the H_2SeO_3 molecule. The corresponding line of $HSeO_3'$ ion appears diffuse at 603 in the biselenite and of SeO_3 radical appears at 734 in the selenite of sodium.

6. Low Frequency Oscillations.

Besides the lines discussed above, there are three lines at 124, 199 and 254 in the solid. Their antistokes are clearly seen in the excitations by the 4047 radiations of the mercury arc. The first two completely vanish on going to solution and the third appears weakly only in the molten state. In the case of iodic acid and iodates,¹⁰ the author has observed similar lines and pointed out some difficulties in assigning them to lattice oscillations as put forward by Gross and Vuks¹¹ to explain the lines discovered by them in the crystals of diphenyl ether, naphthalene, dibromobenzene and benzene. Bhagavantam¹² has suggested that in the latter cases the lines are due to the incomplete rotations of molecules as pictured by Pauling. Recently Sirkar¹³ has investigated the problem more thoroughly and finds that these lines owe their origin to intermolecular vibrations in groups of molecules which persist in some cases in solution and that they are affected by changes of temperature. In view of these discussions, it is probable that the line 254 of the crystals of selenious acid which appears feebly in the liquid state is due to polymerised groups of molecules and the lines 124 and 199 are due to hindered rotation of individual molecules. But a more definite conclusion can be arrived at only by studying the effect of change of temperature on these lines and work in this direction is in progress.

7 Change of State and Raman Effect.

The changes that take place in the main Raman lines of selenious acid as it passes from the solid to the molten state are illustrated in the accompanying

¹⁰ Venkateswaran, C. S., *loc. cit.*

¹¹ Gross and Vuks, *Nature*, 1935, 135, 100, 431, 998; *Jour. de Phys.*, 1935, 6, 457.

¹² Bhagavantam, S., *Proc. Ind. Acad. Sci., A*, 1935, 2, 63.

¹³ Sirkar, S. C., *Ind. Jour. Phys.*, 1936, 10, 109.

plate. Just as in the case of selenic acid¹⁴ the sharp lines of the solid are replaced by broad and intense bands which tend to become narrower in the less concentrated solutions. The extraordinary breadth of these bands is partly explained by supposing that they consist of several components which appear as single, sharp lines in the crystals. But, in general, this feature is characteristic of associated liquids like sulphuric, iodic, formic and acetic acids and therefore, is to be attributed to association of molecules in them. In nitric acid in which there is no association the lines are comparatively sharp. The lines also suffer changes in frequency which is characteristic of hetro-polar compounds. In both selenic and selenious acids this change is pronounced in the lower degenerate vibrations

In conclusion, the author wishes to thank Professor Sir C. V. Raman for his keen interest in the work

Summary.

The Raman spectra of selenious acid as crystals and as aqueous and alcoholic solutions of varying concentrations as well as those sodium biselenite and sodium selenite are investigated. The solid has yielded a spectrum rich in sharp and intense lines, of the following frequencies :—124, 199, 254, 287, 299, 364, 524, 597, 706, 862, 889, 909 and 940 cm^{-1} . The lines broaden out and undergo variations both in frequency shift and intensity.

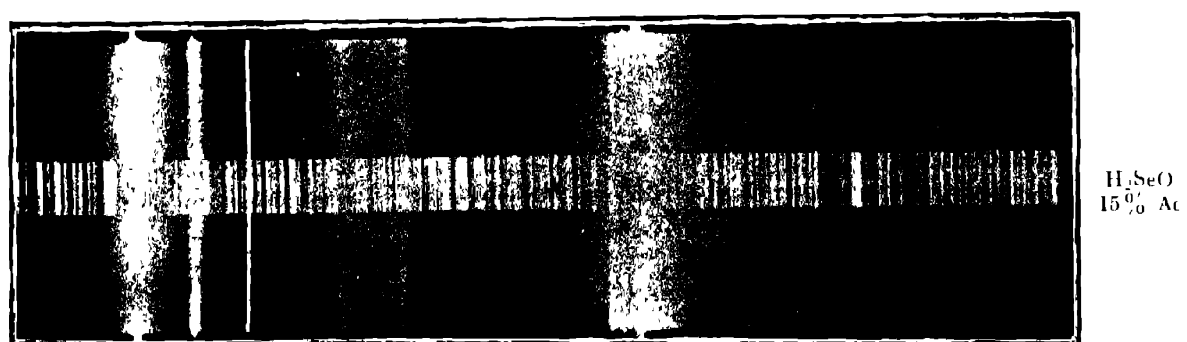
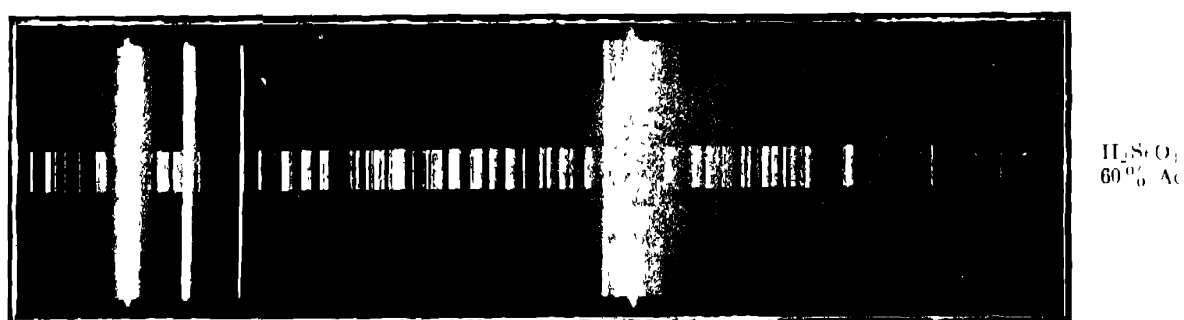
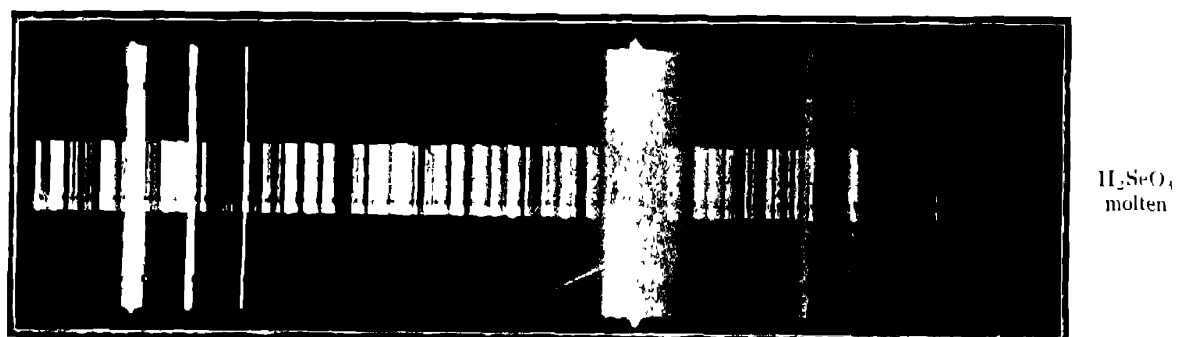
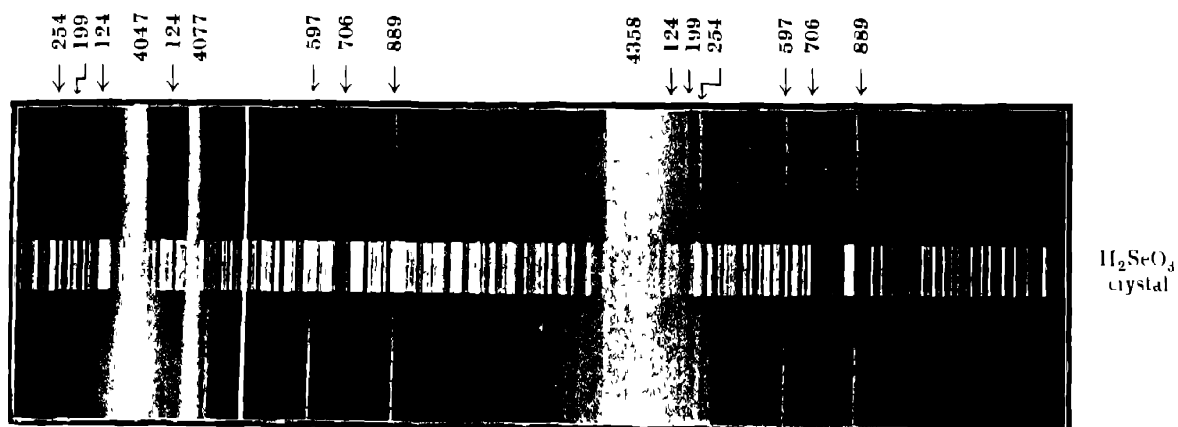
The changes in relative intensities of the two lines, 706 and 597, are particularly remarkable and are explained by postulating two types of molecules namely the symmetrical form $\text{O} = \text{Se} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$ and the unsym-

metrical form $\begin{matrix} \text{O} & & \text{OH} \\ & \diagdown & / \\ & \text{Se} & \\ & / & \diagdown \\ \text{O} & & \text{H} \end{matrix}$ in dynamic equilibrium in the acid. In the

solid and in the solution in methyl alcohol the latter is the more predominant type and in the aqueous solution almost the whole of the acid is converted to the former type. Thus the Raman effect data are made use of for the first time to explain the pseudo or the true nature of the acid

The spectra of aqueous solutions of different concentrations indicate that the dissociation of the acid is weak and that, the proportion of molecules dissociated to HSeO_3' ions remains practically constant throughout. The line 895 is assigned to the HSeO_3' ions. The results are compared to those of its analogue, sulphurous acid. The other lines in the spectrum are attributed to vibrations of definite molecular species by comparing them to the lines in the sodium salts of the acid.

¹⁴ Venkateswaran, C. S., *loc cit*



Raman Spectra

353 ↑ 528 ↑ 695 ↑ 906 ↑

The Raman Spectra of Selenious Acid and Its Sodium Salts 543

Three low frequencies of the solid at 124, 199 and 256 are discussed in the light of the existing theories and their probable assignment is indicated.

The influence of change of state of the Raman spectra of the acid is briefly discussed. The broadening of the lines in the liquid is explained as due partly to association in the molecules and partly to the composite nature of the bands.

RESONANCE CURVES FOR A QUARTZ OSCILLATOR IMMERSED IN LIQUIDS.

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Received May 22, 1936

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

Introduction.

It is well known that resonance for a quartz crystal in air is sharp and is always found not of a symmetrical shape, but steeper towards the higher frequency side. A little broadening on the side of the lower frequency has been explained on the basis that the resistance of the oscillatory circuit changes slightly on tuning to lower frequency for the same circuit, and that such increase in resistance for high frequency current, though small, does affect its shape. Such an effect can be easily demonstrated by the addition of more resistance to the circuit when the resonance curve itself is found to get flatter and less in height. So much so, when the resonance curve is so markedly changed by internal resistance, it was thought that a similar resistance added to the quartz crystal, having the effect of damping its oscillations, might also produce similar or allied changes in the form of the resonance curves. This paper gives results of such experiments carried out with some organic liquids, and the effect of the damping by such liquids on the frequency of the oscillator. Work was also carried out on the relationship between the resonance curve and the diffraction spectra obtained at frequencies, at resonance and near about it.

A. Diffraction Spectra at Resonance and Near about It.

A series of photographs of the diffraction of light by the ultrasonic waves in *o*-xylene (Table VI; Fig. 1) were taken at the resonance frequency of the quartz crystal and at frequencies on either side of it. The radio-frequency current was measured by means of a r.f. milliammeter while the photographs were taken just at those frequencies. Fig. 1 gives these spectra for 5461 \AA with the frequencies and the current marked on either side of each spectrum. It is seen that for maximum current in the oscillatory circuit, *i.e.*, $I_r = 490 \text{ mA}$, when the crystal vibrates at the point of resonance, the frequency is given by $7.33 \times 10^6 \text{ c./s.}$ Thereafter the current diminishes while the frequency also continues to diminish.

With regard to the diffraction spectra, we should naturally expect the number of orders to be a maximum for maximum oscillatory current. But this is found not to be the case. On tuning from a frequency higher than the resonance, it is observed that while the current slowly increases the number of diffraction orders making their appearances also slowly increases. At the resonance frequency of 7.33×10^6 c./s. the number of orders is 3 with a faint fourth. On still further decreasing the frequency the current also decreases, but not so the number and intensity of the diffraction spectra. The maximum number of orders, of 6, occurs at 7.17×10^6 c./s. and for an oscillatory current of only 350 m.a. much less than what it was at the resonance. Visually it was clearly noticed that from the point of resonance to another of lower frequency, the intensity of diffraction spectra increased, and then for still lower frequencies of oscillation, the number and intensity both decreased continuously. In other words, the maximum number of diffraction orders does not coincide with maximum oscillatory current, and it was so, not alone with *o*-xylene for which the photograph is reproduced but for all liquids examined so far. It seems strange that this phenomenon should occur only on one side of the resonance frequency, *i.e.*, always on the side of lower frequency.

B. Resonance Curves in Liquids.

Having found some anomalies regarding the relationship between the oscillatory current and the number of diffraction orders, it became necessary to analyse it completely. Towards that end, resonance curves for the quartz in some typical liquids were taken, liquids of varying viscosity.

In order to get accurately such curves it is necessary that error in the r.f. current should not creep in anywhere to make the results anomalous. The oscillatory current, for any particular frequency, will change, if the anode potential, the filament current or the grid bias should change even by ever so little. Hence precautions to keep these steady and constant were taken at every stage, and for every liquid studied.

The liquids experimented on were benzene, carbon-tetrachloride, carbon-disulphide, anisol, cyclohexanone and glycerine, of which the last member possesses greatest viscosity in the above series, following closely cyclohexanone.

For different points in tuning, the frequencies were determined accurately by a Precision wave-meter, while the oscillatory currents were indicated by a Weston radiofrequency milliammeter of the thermocouple type. Other readings of H.T. voltage, d.c. current were noted to check up the accuracy, from liquid to liquid.

TABLE I. *Benzene*

Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	I^2 \bar{I}_r^2
7.51	110	.050
7.493	175	.128
7.47	260	.282
7.46	330	.454
7.44	400	.666
7.43	445	.825
7.41	490 = I_r	1.000
7.335	445	.825
7.275	390	.634
7.18	350	.511
7.07	310	.400
7.00	260	.282
6.94	200	.167

TABLE II. *CCl₄*

Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	I^2 \bar{I}_r^2
7.53	100	.042
7.50	150	.094
7.48	290	.350
7.46	345	.496
7.448	395	.650
7.41	490 = I_r	1.000
7.35	455	.862
7.265	400	.666
7.13	335	.467
7.03	300	.375
6.96	230	.220

TABLE III. *Carbon-disulphide*

Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	I^2 \bar{I}_r^2
7.53	100	.061
7.50	210	.269
7.48	260	.412
7.46	290	.513
7.448	355	.768
7.41	405 = I_r	1.000
7.335	375	.857
7.255	335	.684
7.13	295	.530
7.052	250	.381
6.98	205	.256
6.92	150	.137
6.89	130	.103

TABLE IV. *Anisol*

Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	I^2 \bar{I}_r^2
7.55	100	.058
7.51	130	.098
7.48	250	.363
7.45	340	.671
7.42	405	.953
7.41	415 = I_r	1.000
7.335	390	.884
7.255	350	.712
7.10	310	.558
6.98	250	.363
6.92	210	.256
6.852	160	.149
6.78	110	.070

TABLE V.
Cyclohexanone

Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	$\frac{I^2}{I_r^2}$
No reading obtainable	220, 230, etc.	
7.598	250	.743
7.51	260	.804
7.480	265	.835
7.41	290 = I_r	1.000
7.10	250	.743
7.012	210	.524
6.948	180	.385
6.91	150	.268
6.812	110	.144
6.78	100	.119

 TABLE VI.
In o-xylene (in Plate XXVII)

No.	Frequency in megacycles per second	Current in the Oscillatory circuit in $m A = I$	$\frac{I^2}{I_r^2}$
1	7.50	180	.135
2	7.478	260	.282
3	7.45	350	.510
4	7.41	450	.843
5	7.33	490 = I_r	1.000
6	7.25	420	.735
7	7.17	350	.510
8	7.04	290	.350
9	6.93	215	.193
10	6.873	150	.094

(For a second quartz crystal)

Tables I to V give the relevant readings of frequencies, with radio-frequency current, in different liquids. To get actually the curves for these liquids in a form for comparison, it is better to take the ratio $\left(\frac{I^2}{I_r^2}\right)$; of the square current at any frequency ($= I^2$) to the square of the current at the resonance frequency ($= I_r^2$), which ratio will be given at the resonance by a value = 1 for all liquids. Then the curves will be uniform and superposable.

Such curves for the liquids investigated are given in Fig. 2

The curves are always much steeper towards the higher frequency, while they spread out on the side of the lower frequency. This is characteristic of all liquids, and indeed so in air also. This is usually explained on the basis that the resistance of the oscillatory circuit is not the same for all frequencies, and that it is higher for lower frequencies. This offers a natural explanation as to why the resonance curves in liquids should be much more spread on the side of lower frequencies. We shall examine the resonance curves for these liquids, each part separately.

Higher frequency range—The curves for benzene, carbon-tetrachloride, carbon-disulphide and anisol are almost steep, but quite distinct with very little separation between each. That for cyclohexanone starts very much

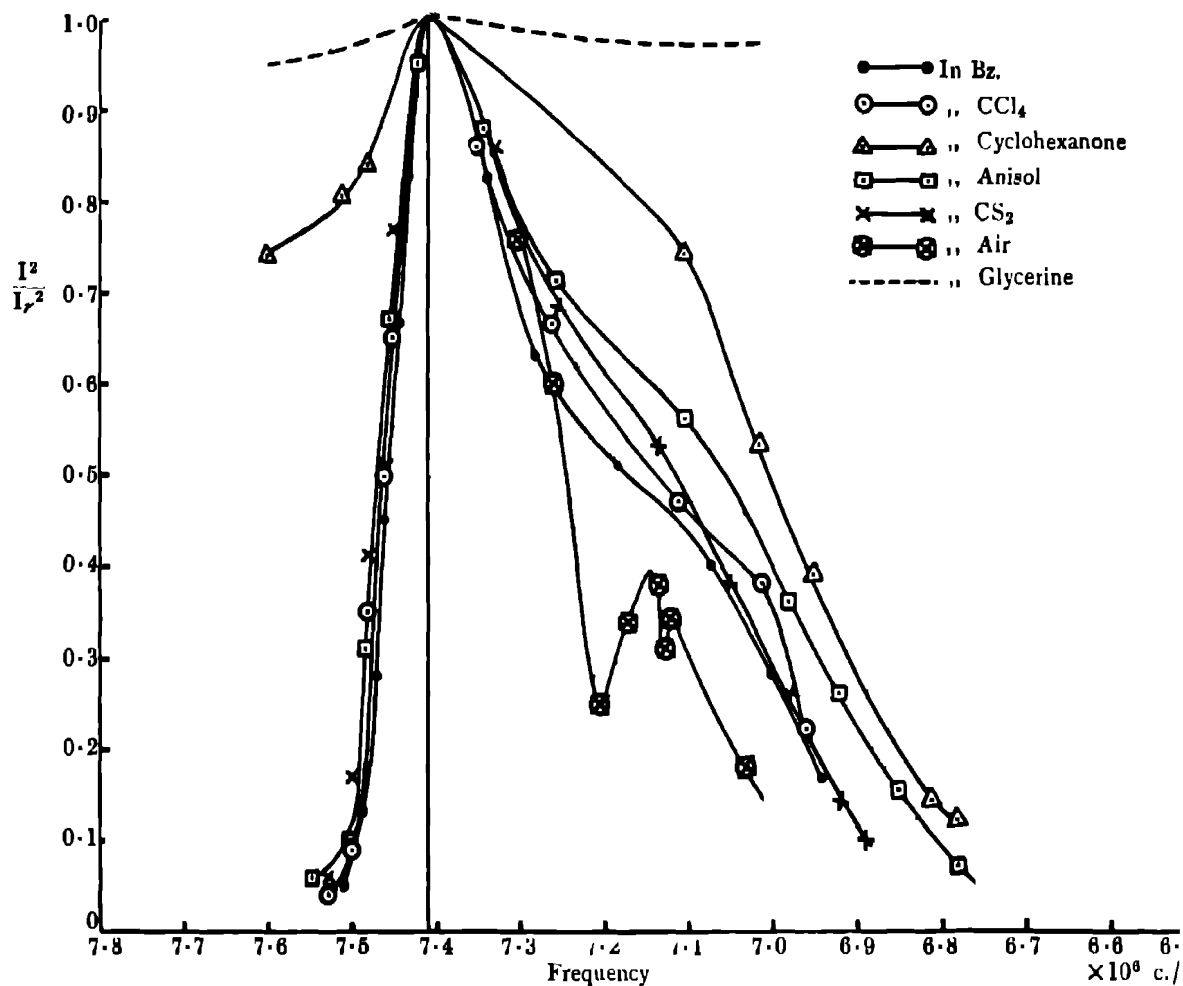


FIG 2.

higher, at $\frac{I^2}{I_r^2} = 0.8$ for a frequency for which the liquids above mentioned have $\frac{I^2}{I_r^2}$ equal to 0.05. For glycerine the corresponding value for $\frac{I^2}{I_r^2} = 0.95$.

Lower frequency range—The curves for each liquid have now become distinct and separate from each other. That for benzene falls rather rapidly while glycerine maintains its top level. Cyclohexanone takes a path midway between these two, while the curves for other liquids fall below that for cyclohexanone. One remarkable feature on this portion of the resonance curves is that, those lines which were crowded on the side of the higher frequency, namely those for benzene, carbon-tetrachloride, carbon-disulphide and anisol, are here clearly resolved and separated.

If we now compare the viscosities for these liquids, with say, the ratio of $\frac{I^2}{I_r^2}$ for a frequency 7.20×10^6 c./s. at which point they are all resolved, we find these curves, surprisingly enough to follow the same order as that for viscosities. Benzene with lowest viscosity (except CS_2) has a high

gradient, while glycerine shows almost no gradient, it possessing the highest viscosity in this series. All liquids follow this order. Here it may be remarked that for some reason yet unknown carbon-disulphide behaves anomalously.

TABLE VII.
Viscosity and Damping

No	Liquids	Viscosity at 25°C. (from I C T)	$\frac{I^2}{I_r^2}$ at 7.20×10^8 c./s. (from fig. 2)	Oscillatory current in m A (shown in fig. 2)
1	Benzene ..	0.00604	0.53	490
2	Carbon-tetrachloride ..	0.008876	0.57	490
3	Carbon-disulphide ..	0.00356	0.61	405
4	Anisol ..	0.0101	0.65	415
5	Cyclohexanone ..	0.028	0.86	290
6	Glycerine ..	8.2	0.98	< 30

These facts are brought forward separately in Table VII and the agreement between the observed order of resolution of these curves and the order of viscosity is good. It is very clear now that the lower frequency portion of the resonance curve is very deeply connected with the nature of the liquid, more especially its viscosity, and work, of the nature of, diffraction of light by ultrasonic waves, carried out in that part of the curve will, it is hoped, give more information regarding the nature of the liquid and the effect of damping.

C Effect of Damping

It is pertinent to enquire at this stage whether any effect due to damping was observed or not. There are two distinct effects to be expected from damping: (a) a shift in the frequency and (b) a lowering of the amplitude of vibration, and directly here, lowering of the supersonic intensity. In the audible range, effect due to (a) is negligible and ordinarily it is not noticed while (b) under certain conditions can be detected. Ultra-sonic range is especially suited for noticing both the effects under (a) and (b).

Case (a):—The experimental arrangement required a slight modification of the technique. The quartz crystal was as usual suspended between two metal contacts and held in a particular position without disturbance. Having obtained a certain frequency of vibration, the entire apparatus was

left undisturbed, without even touching any part. The tall vessel containing the liquid was slowly raised from just underneath the crystal, till one side of the quartz piece was well under the liquid. The crystal as a whole was not immersed. Now the crystal was set into vibration, with current and voltage properly adjusted; and the electrical wave-length was carefully measured by means of a Precision wave-meter. The trough was lowered and the liquid removed for experimenting with another liquid. The quartz piece was carefully washed, *in situ*, with volatile solvents, without in any way disturbing the arrangement. Readings for frequencies, with quartz in other liquids, were taken in the same way. To see that it was not in any way disturbed, the frequency of oscillation of the quartz in air was taken every time, before and after each experiment, and it was faithfully reproduced every time, being the same as the one in the very beginning. Hence it was concluded that no external disturbance could have affected the frequency, and any change observed was due to the damping effect in the liquid and to it alone.

The frequency of vibration was taken first in air; and then in the following liquids: benzene, toluene; *o*-, *m*- and *p*-xylenes; carbon-tetrachloride, carbon-disulphide, anisol; and cyclohexanone. Table VIII gives the frequencies as obtained in this set of experiments.

TABLE VIII
Shift in Frequency due to Damping

No.	Liquids	Frequency in megacycles per second (measured by wave-meter)	Damping co-efficient (standard = air)
1	Benzene ..	7.285	0.715×10^6
2	Toluene .	7.285	"
3	<i>o</i> -xylene ..	7.285	"
4	<i>m</i> -xylene ..	7.285	"
5	<i>p</i> -xylene ..	7.285	"
6	Carbon-tetrachloride ..	7.280	0.764×10^6
7	Carbon-disulphide ..	7.280	"
8	Anisol ..	7.280	"
9	Cyclohexanone ..	7.262	0.920×10^6
10	In air ..	7.320	Standard

It is well known that if we know the two frequencies, with and without damping, k the co-efficient of damping can be easily calculated from the

formula

$$n' = \sqrt{n^2 - k^2}$$

where n' is the damped frequency and n the natural frequency. Column 3 in the table gives the co-efficients of damping as calculated by this formula, with the frequency of oscillation in air as the standard.

It appears from these results that damping from air to liquids generally is considerable, as seen from the diminution in frequency from 7.320×10^6 c./s. to 7.285×10^6 c./s. But between liquids themselves, when there is great difference in viscosity, as between benzene and cyclohexanone or glycerine, then again there is a small diminution in the frequency. The table shows these effects very clearly

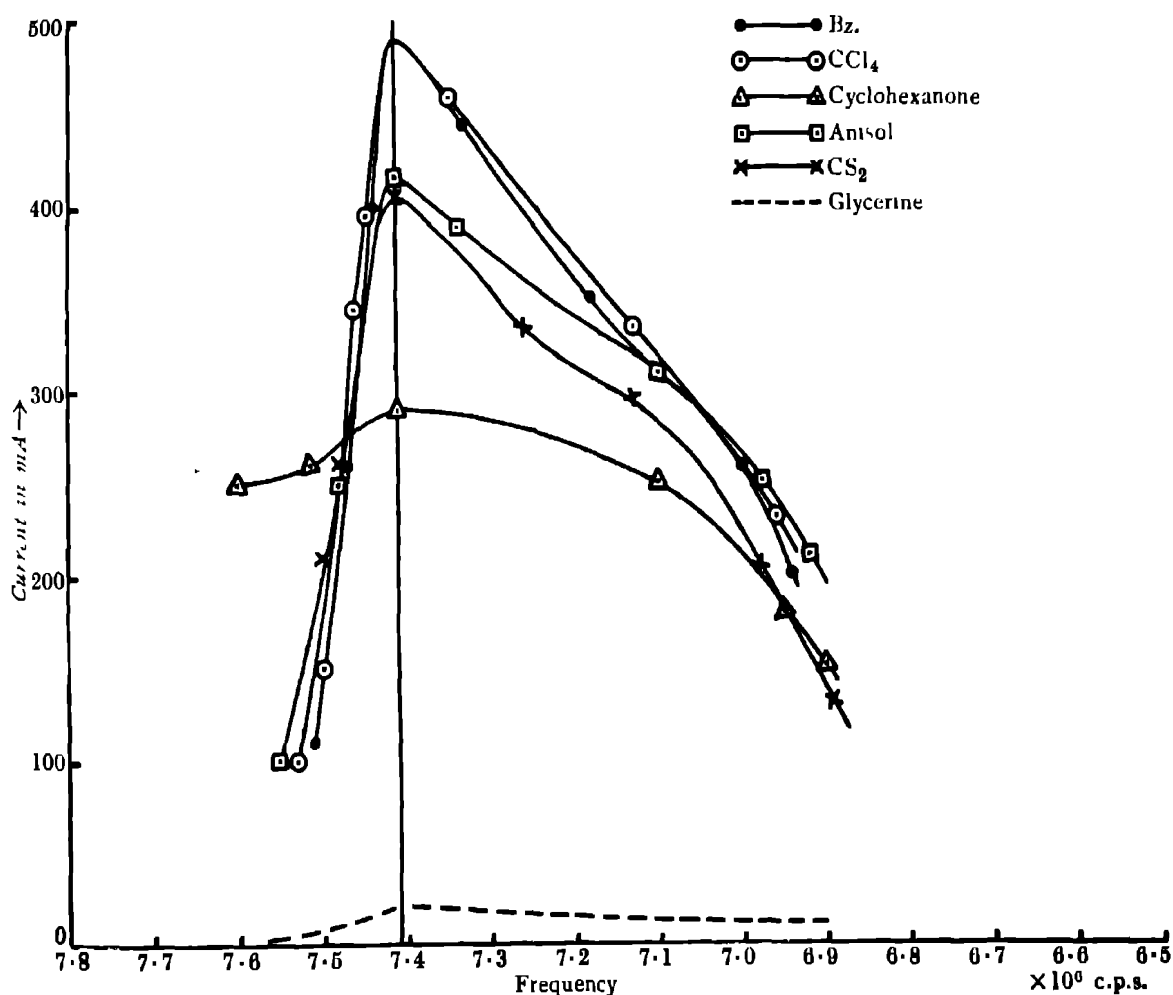


FIG. 3.

Case (b) :—Fig. 3 gives the relation between frequency at resonance and near about it, and the oscillatory current. The damping, as measured by the current is also indicative of the diminution in supersonic amplitude, The

current is less for more highly viscous liquids, such as cyclohexanone and glycerine, and the curves are also more flat. Tables I to V give the results.

The conditions are true if the quartz crystal has one face immersed in the liquid. It was thought desirable to see whether the damping increased with depth, to which depth the crystal was immersed, for then we know that the effective damping is increased at greater depths. The following table (Table IX) gives the relation between the depth, the frequency and the damping co-efficient. It is clear that damping increases with depth, as is to be expected.

TABLE IX.
Effect of Depth on Damping : in Toluene.

	Depth in cms of the Quartz crystal	Frequency in mega-cycles per second	Damping co-efficient
1	One surface in contact with liquid ..	7.285	Standard
2	Quartz just immersed ..	7.250	0.714×10^6
3	Quartz, 2 cms. below surface ..	7.210	1.043×10^6
4	Quartz, 4 cms below surface ..	7.160	1.345×10^6

D. Range and Sharpness of Resonance.

It is known from the work of Barton and others, that there are two features to be distinguished in any resonance curve, namely, (1) the range and (2) the sharpness. The curve is sharper for less damping, while the range becomes less at the same time. Also, the curve is much sharper at higher frequencies than for lower, when the liquid used for damping the vibrations is the same.

Fig. 2 gives the resonances in a number of liquids of varying damping co-efficients. It is seen from the curves that for liquids of greater viscosity—and therefore greater damping—the range is greater and not sharp at all. This is seen to be so for glycerine and cyclohexane. The range for the same amplitude $\frac{I^2}{I_r^2} = 0.75$, is 7.10 to 7.58 megacycles for cyclohexane, while it is only 7.30 to 7.43 megacycles for benzene. Fig. 3 gives an idea of the flatness of the curves.

Another point of interest is to get resonance curves for different harmonics of the crystal in the same liquid—whereby damping is kept constant—and compare the range and sharpness of such curves at different frequencies.

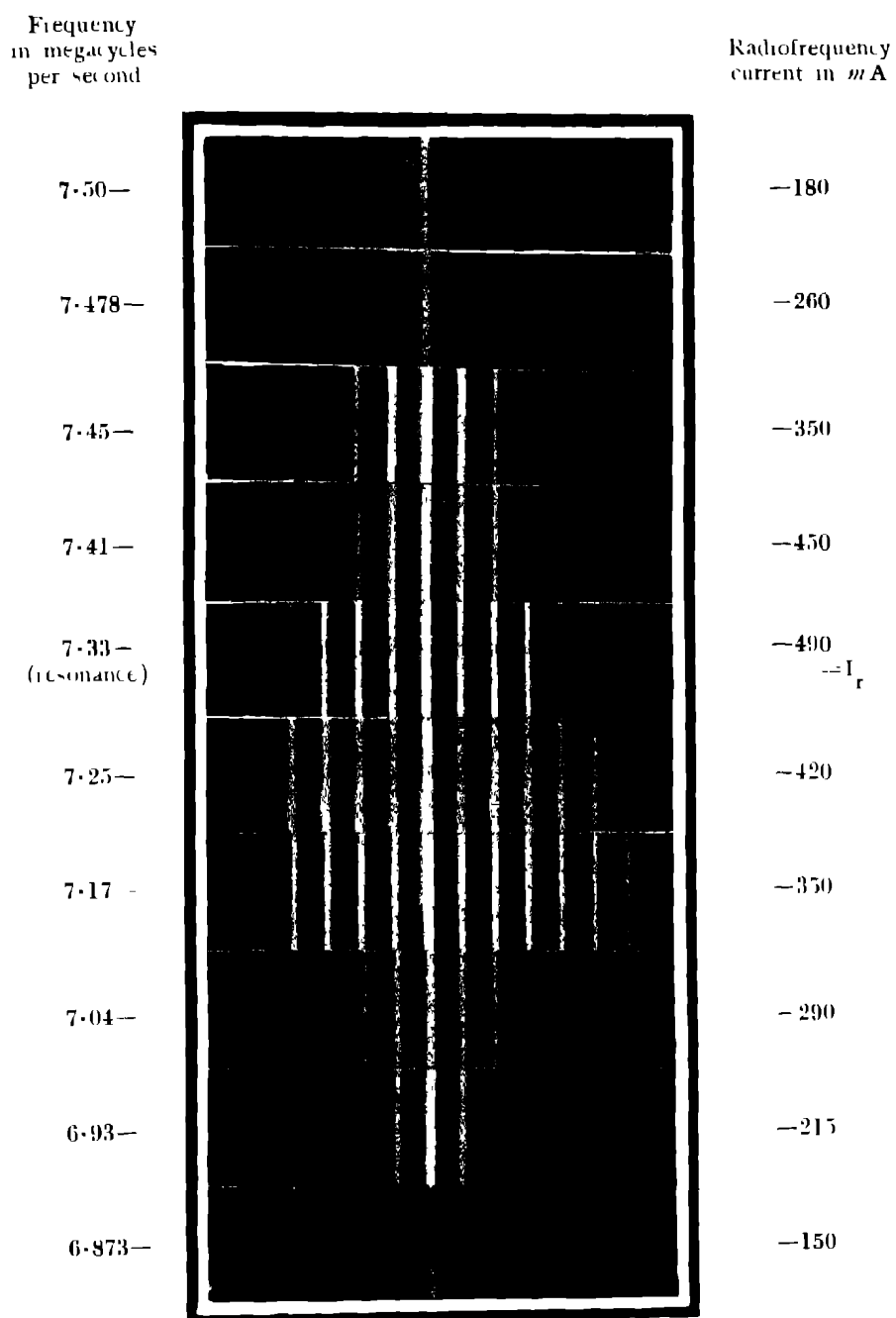


FIG. 1 Diffraction spectra in *o*-Xylene near the resonance frequency of a quartz oscillator (for 5461 Å).

Theory shows that the resonance at higher frequencies must be much sharper than at lower frequency, when the damping is constant. Benzene was chosen as the liquid for the quartz oscillator and a frequency of $20 \cdot 00 \times 10^6$ c./s. was employed as the higher harmonic. It was found that the resonance was very sharp and its range did not extend much, as it was found that even a slight disturbance was enough to make the diffraction spectra, produced by the crystal oscillating in the liquid, disappear. The oscillatory current was also taken as an indicative. This is only qualitative, as even an exact quantitative measurement will not be comparable with the one at $7 \cdot 41 \times 10^6$ c./s., since the conditions of experiment will not be identical. The resistances of the circuits, which are important factors in such resonance curves, will not at all be comparable. But, withal, a qualitative test was found to be in agreement with theory.

The general ideas developed regarding the range and sharpness of resonance curves are found to hold good in the region of ultrasonics.

The author records his grateful thanks to Prof. Sir C. V. Raman for constant interest in the work.

Summary.

The paper gives results of investigation with regard to the resonance curves of a quartz oscillator immersed in liquids. Each curve is characteristic of the liquid and is resolved one from another very clearly only on the lower frequency region of the curve. The order of resolution observed is the order of the viscosities of the liquids. It was also noticed that a greater number of diffraction orders was observed, not at the resonance of the crystal, but at a point of lower frequency, corresponding to the region of clear resolution of the resonance curves. The effects of damping, namely (1) a shift in frequency and (2) flatness of the resonance curve are observed and recorded. The range and sharpness of resonance have been compared (a) as between different liquids of different damping co-efficients at a given frequency, and (b) in one liquid but at different frequencies (higher harmonics). For condition (a) range extends while the sharpness diminishes for highly viscous liquids, while for condition under (b) the sharpness increases with diminished range at higher frequency.

ROTATIONAL ANALYSIS OF THE ÅNGSTRÖM BANDS AT λ 6080 AND 6620 Å.U.

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THE Ångström bands of CO, though simple in structure, inasmuch as they are due to the transition $B^1\Sigma \rightarrow A^1\Pi$, have evoked considerable interest from more than one point of view. The rotational analysis of some of these bands was given by Hulthen.¹ The 0-0 and 1-0 bands were analysed by Jassé,² by Johnson and Asundi³ and by Rosenthal and Jenkins.⁴ The latter were able to show that pronounced perturbations of the rotational levels occurred in the bands they analysed, viz., bands having $v'' = 0, 1, 2$ and 3, and especially in bands with $v'' = 0$ and 1, these perturbations occurred at relatively low J values in addition to perturbations at high J values observed in all bands. The displacements of the 0-1 and 1-1 bands previously observed by Johnson and Asundi was traced to this rotational perturbation very near to the origin in these cases. All these perturbations are definitely shown to be in the $A^1\Pi$ level. Further proof of this fact is given by similar perturbations observed by Read⁵ in such of the fourth positive carbon bands as have initial levels of the same quantum number as the final levels of the Ångström bands. The initial state $B^1\Sigma$ of these latter bands is also not without interest. Recently, Coster and Brons⁶ have reported a sudden decrease in intensity of some of the rotational lines which they attribute to pre-dissociation of the molecule. The present paper deals with the rotational analysis of the 0-4 and 0-5 bands, preliminary results of which have been published before.³ Measurements have been made on plates taken in the first order of a 21 ft concave grating. The spectrum was produced in a usual discharge tube of CO and the data are confined to relatively low J values on account of the low temperature production of the bands.

Tables I and II contain the analysed wave-numbers (cm^{-1}) *in vacuo* of the lines of the two bands. Table III contains the $\Delta_2 F'(J)$ values observed in these bands and those calculated by Rosenthal and Jenkins. On account of the Λ -type doubling in the lower level, combination defects are to be expected, but these are negligible in such at least of the bands as are free from perturbations at low J values. Table IV gives the $R(J) - Q(J)$

and $Q(J + 1) - P(J + 1)$ values which should be equal if no combination defects were present, these being then $\Delta_1 F'(J)$ values; also similarly the $R(J) - Q(J + 1)$ and $Q(J) - P(J + 1)$ values which would be $\Delta_1 F''(J)$.

The agreement between the observed and calculated values of $\Delta_2 F'(J)$ in Table III is quite satisfactory and affords proof of the correctness of the analysis. Reference to Table IV shows that combination defects are negligible for the 0-5 band at λ 6620. This indicates that there are probably no perturbations in this band upto the J values here observed. In order to ascertain this, the method used by Rosenthal and Jenkins of plotting deviation curves was adopted. Formulæ were developed to express the regular lines of each branch in the bands by the method of least squares and the observed *minus* calculated values were graphically plotted. The small residuals for the band at λ 6620 (the maximum $O-C$ values being $+0.22$ for $P(1)$, $+0.20$ for $Q(13)$ and $+0.18$ for $R(3)$, indeed confirm that there are no perturbations in this band inside the observed limit. This is further corroborated by the recent work of Gerò¹³ on the fourth positive carbon band ($v' = 5$, $v'' = 13$), which involves this same level. The first strong perturbation observed by Gerò at $Q(30)$ is already outside the limit of the present observations. On the other hand, the band at λ 6080 shows considerable combination defects and correspondingly large residuals for the P and R branches, the Q branch, however, being more or less normal. The residuals increase towards small J values starting from $+0.06$ at $P(6)$ to $+0.94$ at $P(2)$ and from $+0.06$ at $R(6)$ to $+1.04$ at $R(2)$, and therefore point to $J = 0$ being perturbed as in the 0-1 or 1-1 bands, the perturbation being smaller than and opposite in sign to that observed in the latter bands. This perturbation, though small, appears to be genuine because firstly while $\Delta_2 F'(J)$ values are proper, the combination defects are appreciable and secondly, the positive residuals increase towards $J = 0$ thus indicating a violet shift of the origin which has been already noticed.³ Incidentally, a second perturbation at $P(19)$ is indicated by the residuals, -0.28 , -0.52 and -0.43 for $P(18)$, $P(19)$ and $P(20)$ respectively.

Coster and Brons¹² find a perturbation in this band at about $J = 31$ for this level but Gerò¹³ has shown, from a study of the Herzberg and the fourth positive carbon bands involving this level that perturbations occur at $J = 0$, 23 and 37. The present results confirm the perturbation at $J = 0$ but the data are not sufficient to confirm the other perturbations. The very small perturbation at about $J = 19$ has not been recorded previously and may not be real.

Rosenthal and Jenkins⁴ have come to the conclusion that the perturbations are caused by the rotational terms of the electronic state $a^3\Pi$. Watson⁷

from Zeeman effect results also favours this interpretation. Coster and Brons^{1a} classify them as due to the already known states $a'^3\Sigma^+$ and $d^3\Pi$ and to certain $e^3\Sigma^-$ and $^1\Pi$ states which are still unknown. In view of the multiple perturbations in each band, such an explanation appears quite plausible. Except for the hypothetical $^1\Pi$ state, all perturbing levels would then, however, be triple. This creates a theoretical difficulty pointed out by them, which concerns the condition that for the two terms to perturb they must have the same symmetry with respect to interchange of the point co-ordinates of the electrons, that is, they must be terms of equal multiplicity.⁸ There is, however, a possibility of explaining some of these perturbations as due to the ground $X^1\Sigma$ state of the molecule. It is of course not possible to extrapolate with much accuracy but if we do so from the equation given by Read⁵ for the fourth positive carbon bands, we obtain for the vibrational terms of the ground level, values which are comparable with those of the $A^1\Pi$ state which is perturbed, as in the following table :—

$X^1\Sigma$ Level		$A^1\Pi$ Level	
v	Energy cm.^{-1}	v	Energy cm.^{-1}
		0	65809
40	66865	1	67297
41	68006	2	68739
42	69124	3	70151
43	70217	4	71527
44	71288	5	72869

If the extrapolation gave correct values, from this table one would expect that of all levels, only $v = 3$ of $A^1\Pi$ state would exhibit near $J = 0$, a perturbation due to $v = 43$ of $X^1\Sigma$ state. This, however, has no support from experimental evidence and therefore the coincidence is simply fortuitous and the extrapolation is certainly only approximate. We know, however, that $v = 1$ of $A^1\Pi$ state is perturbed near $J = 0$ and if we assume that this perturbation is caused by $v = 40$ of $X^1\Sigma$ state, it is possible that a similar perturbation near the origin at $v = 4$ of the $A^1\Pi$ state is caused by $v = 44$ of the $X^1\Sigma$ state within the errors of extrapolation. It appears as if some of the perturbations, therefore, are definitely due to the ground level of the

TABLE I.

Analysis of 0-4 Band at λ 6080 Å.U.

(Figures in brackets denote estimated Intensities.)

J	P-Branch	Q-Branch	R-Branch
1	16450.48 (6)
2	16444.81 (0)	452.37 (2)	16464.10 (0)
3	443.52 (6)	454.97 (3)	470.71 (1)
4	443.13 (3)	458.53 (4)	478.13 (1)
5	443.52	462.95 (4)	486.45 (2)
6	445.01 (5)	468.25 (8)	495.61 (2)
7	447.33 (4)	474.49 (8)	505.67 (2)
8	450.48	481.48 (8)	516.64 (2)
9	454.50 (4)	489.41 (7)	528.43 (2)
10	459.36 (3)	498.19 (7)	541.09 (2)
11	465.06 (4)	507.84 (7)	554.59 (2)
12	471.73 (3)	518.39 (7)	
13	479.21 (3)	529.82 (7)	
14	487.63 (2)	542.01 (5)	
15	496.84 (2)	555.21 (5)	
16	506.95 (2)		
17	518.14 (1)		
18	529.82		
19	542.55 (0)		
20	556.32 (0)		

TABLE II.

*Analysis of 0-5 Band at λ 6620 Å U.**(Figures in brackets denote estimated Intensities.)*

J	P-Branch	Q-Branch	R-Branch
1	15104.24 (0)	15108.07 (1)	15115.62 (1)
2	102.12 (1)	109.93 (2)	121.67 (0)
3	100.89 (5)	112.72 (5)	128.24 (2)
4	100.89	116.38 (5)	135.86 (2)
5	101.50 (3)	121.00 (7)	144.41 (4)
6	103.17 (7)	126.55 (8)	153.87 (3)
7	105.73 (5)	132.96 (8)	161.15 (4)
8	109.20 (8)	140.38 (10)	175.43 (3)
9	113.59 (6)	148.62 (8)	187.61 (4)
10	118.90 (6)	157.83 (9)	200.68 (4)
11	125.14 (5)	167.97 (8)	214.70 (4)
12	132.36 (5)	179.03 (6)	(masked by H α)
13	140.38	191.02 (6)	245.53 (2)
14	149.45 (5)	203.90 (5)	
15	159.29 (3)	217.86 (6)	
16	170.24 (3)	(masked by H α)	
17	182.06 (2)	248.20 (6)	
18	194.79 (1)	264.69 (5)	
19	208.47 (0)	282.26 (7)	

TABLE III.

 $\Delta_2 F'(J)$ Values.

Calculated Values are from Rosenthal and Jenkins (l.c.).

J	Observed R(J) - P(J)		Calculated
	$\lambda 6080 \text{ Å U}$	$\lambda 6620 \text{ Å.U}$	
1	..	11.38	11.62
2	19.29	19.55	19.47
3	27.19	27.35	27.26
4	35.00	34.97	35.05
5	42.91	42.93	42.83
6	50.60	50.70	50.62
7	58.34	58.42	58.40
8	66.16	66.23	66.18
9	73.93	74.02	73.96
10	81.73	81.78	81.74
11	89.53	89.56	89.51
12	97.27
13	..	105.15	105.04

molecule. It is further likely that the state K at 38820 cm^{-1} , discovered by Kaplan⁹ is responsible for some of the perturbations. The band which involves this state is reported to possess a structure similar to the fourth positive carbon bands. Therefore it is probable that K is a singlet level.

In addition to perturbations, the Ångström and certain other bands of the CO molecule are reported to exhibit the phenomenon of predissociation.¹⁰ Brons has recently given¹¹ an interpretation of this and attributes the predissociation in the Ångström bands as due to a molecular term arising out of $C(^1S) + O(^3P)$. This term can only be a triplet term which according to

TABLE IV.
Term Differences.

J	$\lambda\ 6080\ \text{\AA.U.}$				$\lambda\ 6620\ \text{\AA.U.}$			
	$\Delta_1 F'(J)$		$\Delta_1 F''(J)$		$\Delta_1 F'(J)$		$\Delta_1 F''(J)$	
	$R(J) - Q(J)$	$Q(J+1) - P(J+1)$	$R(J) - Q(J+1)$	$Q(J) - P(J+1)$	$R(J) - Q(J)$	$Q(J+1) - P(J+1)$	$R(J) - Q(J+1)$	$Q(J) - P(J+1)$
0	3.83
1	7.55	7.81	..	5.95
2	11.37	11.47	..	8.85	11.74	11.83	5.69	9.04
3	15.74	15.40	9.13	11.84	15.52	15.49	8.95	11.83
4	19.60	19.43	12.18	15.01	19.48	19.50	11.86	14.88
5	23.50	23.24	15.18	17.94	23.41	23.38	14.86	17.83
6	27.36	27.16	18.20	20.92	27.32	27.23	17.86	20.82
7	31.18	31.00	21.12	24.01	31.19	31.18	20.91	23.76
8	35.16	34.91	24.19	26.98	35.05	35.03	23.78	26.79
9	39.02	38.83	27.23	30.05	38.99	38.93	26.81	29.72
10	42.90	42.78	30.24	33.13	42.85	42.85	29.78	32.69
11	46.75	46.66	33.25	36.13	46.73	46.67	32.71	35.66
12		50.61	36.20	39.18	..	50.64	35.67	38.65
13		54.38		42.19	54.51	54.45	..	41.57
14		58.37		45.17	..	58.57	41.63	44.61
15				48.26	47.62
16					..	66.14
17					..	69.90	..	53.41
18					..	73.79	..	56.22

Kronig's theory⁸ should not perturb or predissociate the singlet level $B^1\Sigma$ of the Ångström bands. Similarly, most of the other correlations that he gives indicate a direct violation of the selection rule. We believe that these predissociations, if real, have to be explained in a different way, especially in view of the very low value for the energy of dissociation which comes out by this correlation. We intend to discuss this in detail in a separate communication.[†]

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[†] This number p. 562.

ON THE DISSOCIATION ENERGY OF CARBON MONOXIDE.

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AND

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THE energy of dissociation of the CO molecule has been the subject of a discussion since some time past. Quite recently Herzberg¹ has pointed out certain objections against the low value of 8.41 volts for $D(\text{CO})$ given by Coster and Brons². On the other hand, Schmid and Gerö³ still more recently have suggested a much lower value of 6.9 volts for $D(\text{CO})$. All these various values have been based on data of rotational pre-dissociation and we have therefore thought it desirable to point out some more objections both of an experimental and a theoretical nature.

Rotational predissociation is in general recognised by an abrupt disappearance of the individual band lines. But the converse is not always true, because such a disappearance may be brought about simply by experimental conditions, *i.e.*, by factors which have nothing to do with pre-dissociation like the intrinsic intensity of the band, the method of production depending on temperature, the sensitivity of the plate, the time of exposure etc. Indeed the predissociation at 9.66 volts above the ground level obtained by Coster and Brons and on which they very definitely based the value of 8.41 volts for $D(\text{CO})$, has been shown to be an instance of this kind. Whereas Brons did not obtain lines higher than $J = 17$ in the three bands of the fourth positive group, which he measured, Gerö⁴ obtained for the two of these bands which he measured, lines up till about $J = 34$. This significant observation not only invalidates the value of 8.41 volts for $D(\text{CO})$ but also strengthens our viewpoint that the other observations of decrease of intensity, which are ascribed to predissociation, might also arise from similar causes especially the one⁵ found in $b^3\Sigma$. Other instances of a similar kind are the Herzberg and Ångström bands in which earlier workers⁶ could only measure lines up to about $J = 25$ whereas recent work under different methods of production shows that it is possible to obtain lines with higher rotational quantum numbers. The intensity distribution especially in these bands is

furthermore complicated and rendered chaotic by a large number of extraneous lines which Coster and Brons⁷ take for CO₂ bands, but which evidently belong to the CO bands of the system $a' {}^3\Sigma \rightarrow a {}^3\Pi$. Therefore such slight irregularities cannot be called abnormal and the intensity distribution of the (0, 0) Ångström band shown in the reproduced microphotometer plate⁷, to our mind, requires further experimental confirmation on account of the numerous extraneous lines. Similar remarks apply to the decrease in intensity observed in the other Ångström band and the Herzberg bands⁸. It seems therefore doubtful, whether the dissociations at 11.54 and 11.08 volts are already definitely established.

Assuming, however, that some of these cases of intensity decrease come out to correspond to a dissociation of the molecule, the further questions arise, whether it is a case of real predissociation or the ordinary dissociation by instability of the molecule brought about by rotation. Only the former case means an improvement on the usual vibrational extrapolation. An example is furnished by S₂. The value for D (S₂) obtained from the interpretation of the abrupt termination of the rotational structure in two successive vibrational levels does not agree, as we have pointed out recently⁹ at greater length, with the value obtained from the convergence point, whatever products of dissociation are assumed for the upper electronic term. Indeed, as far as CO is concerned, it is rather surprising that most of the various predissociations would at the same time mean a violation of the selection-rule in Kronig's theory of rotational predissociation¹⁰. It is sometimes assumed that such a violation is observed¹¹ in the spectrum of P₂ but even here it does not appear to be definitely established because the argument is based on the extrapolated values of the energy of dissociation of P₂ and of excitation of P which themselves are somewhat uncertain. If, however, the interpretation in the P₂ molecule is correct, it can mean only an exception to the general rule, and such exceptions can hardly be so numerous as they would be in the case of CO.

Predissociation data always give an upper limit to the energy of dissociation because they involve a certain amount of kinetic energy, which may be small or great depending upon the steepness of the repulsive curve. An exact correlation of values obtained from such data to the levels of the separated system is not to be expected and hence the existence of such exact correlation does not establish a true case of predissociation. We may illustrate it by the value of 9.66 volts of Brons, which lies 1.42 volts below 11.08, and corresponds exactly to the excitation energy of the C atom but just this value of 9.66 volts has been proved to be incorrect.

Herzberg has already pointed out¹, that the energy difference of about half a volt between the two predissociations in $C^1\Sigma$ and $B^1\Sigma$ can be explained as a true difference between terms of the separated systems only in a very artificial way and is inclined to take this amount as an excess of kinetic energy. If we assume that Kronig's selection rule is strictly valid, we shall have to explain both of these predissociations by repulsive curves originating in $C(^3P) + O(^3P)$ or $C(^1D) + O(^1D)$ (being the next higher) because only these combinations can give rise to singlet terms. In the latter case $D(CO)$ becomes 7.86 volts, a value which appears to be too low on account of thermochemical reasons, discussed later. In the former case 11.08 volts will represent $D(CO)$ *plus* a certain amount of kinetic energy, whose magnitude will depend on the correct value of $D(CO)$ itself. We believe $D(CO)$ to be roughly 10 volts, in which case the excess of kinetic energy would be about 1 volt. Schmid and Gerö³ report another predissociation at 9.57 in $A^1\Pi$, but details about this are not yet available and we cannot say whether our general objections against predissociation values in CO will hold good also in this case. If it is a true case, $D(CO)$ will be about 9.5 because this predissociation takes place again in a singlet level. On this view, the excess of kinetic energy for the upper one will be about one and a half volts. This rather large amount of kinetic energy can be avoided by one or other correlations, suggested by other authors, but only at the expense of the selection rule and on the assumption, except for Herzberg, that predissociation data invariably give exact values. We prefer, however, to take this excess of kinetic energy as genuine because it is obvious, that among the 18 molecular terms arising from a combination of $C(^3P) + O(^3P)$ quite a large number will be repulsive states. Since they are not degenerate and therefore possess varying slopes and since already a single one of them will intersect various electronic states at different internuclear distances according to their heights above the ground level, we do not see any difficulty in explaining this increasing excess of kinetic energy from level to level, according to the present interpretation.

From considerations of the existence of only one or two vibrational levels in the state $b^3\Sigma$, a value of $D(CO) = 10.45$ volts has been deduced¹². This will be the upper limit. If the new predissociation in $A^1\Pi$ is proved, this will be reduced to 9.57 volts. A value of this order of magnitude for $D(CO)$ is to be expected from considerations of thermochemical data on account of its intimate connection with the heat of sublimation of carbon. Herzberg has already pointed out, that the data of thermochemistry give a lower limit for $D(CO)$. We should like to add, that also the energy of the C—H bond would be reduced following a reduction in $D(CO)$ and $S(C)$.

Since free CH_3 radicals react rather rapidly with H_2 to form $\text{CH}_4 + \text{H}$ the C—H bond cannot have very much lower energy¹³ than D (H_2), which means that S (C) cannot have a much lower value than 150 Kcal/mol and D (CO) a value not much lower than 10 volts.

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DISPERSION OF DEPOLARISATION OF RAYLEIGH SCATTERING.

Part I. Fatty Acids.

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1 Introduction.

ALTHOUGH the state of polarisation of the light scattered transversely by a variety of substances has been studied in detail by numerous investigators, comparatively little work has been done on the dispersion of depolarisation with wave-length. Some early investigations carried out by K. S. Krishnan¹ on a large number of liquids using sunlight filtered through suitable coloured glasses did not show any large dependence of depolarisation on wave-length. These measurements should be taken as only preliminary, since the incident light was not strictly monochromatic, filters used transmitting fairly wide regions of the spectrum. A few years later K. S. Krishnan and A. Sircar² have reported the results of the measurements on the dispersion of polarisation of the light scattered by benzene both in the liquid state and in the state of vapour. It is found that while the depolarisation factor for the liquid remains constant over a wide range of wave-length the value for the vapour increases appreciably as we proceed towards the ultraviolet.

A. F. Turner³ has studied in detail the dependence on wave-length of the intensity and depolarisation of the light scattered transversely by liquid benzene. But no appreciable dispersion of depolarisation has been reported by him. Very recently the depolarisation of the unmodified scattered light has been investigated by S. M. Mitra⁴ in carbon disulphide and benzene over a wide range of wave-length, and it is found that the depolarisation factor is independent of wave-length for these two liquids. The investigators mentioned above restricted themselves to observations with a non-associated

¹ K. S. Krishnan, *Phil. Mag.*, 1925, **50**, 697.

² K. S. Krishnan and A. Sircar, *Ind. Jour. Phys.*, 1931, **6**, 193.

³ A. F. Turner, *Inaugural Dissertation, Berlin University*, 1935.

⁴ S. M. Mitra, *Zeits. f. Phys.*, 1935, **96**, 29.

liquid such as benzene. Consequently in the absence of adequate data it is not justifiable to say that the depolarisation of the transversely scattered light is independent of wave-length. It has been observed that highly associated liquids show certain anomalies in light scattering⁵. Therefore it is not unreasonable to expect an appreciable dispersion of depolarisation in these liquids. In view of these circumstances, it was thought desirable to study the dependence of depolarisation of the unmodified scattering on wave-length in a series of associated as well as non-associated liquids. In this paper the results obtained with the first five members of the fatty acids and benzene are given.

2. *Experimental Details.*

The principle of the method is essentially the same as in the well-known Cornu method of measuring partially polarised light which has been very frequently used in light scattering, with this difference, *viz*, the scattered light after passing through the double-image prism and nicol is analysed spectroscopically. A fused silica cross was used as the container for the liquid to be examined. The arms of the cross were each 3 inches long and $1\frac{1}{2}$ inches in diameter with fused transparent quartz windows fused on to their ends. The cross was connected on to a pyrex flask through a quartz pyrex seal. The liquid was distilled dust free into this cross by the usual method of Martin. Chemically pure liquids were taken for the experiment. The cross was blackened on the outside excepting for three end faces.

The light from a point-light quartz mercury arc lamp was focussed at the centre of the silica cross containing the dust-free liquid. A quartz double-image prism (optical contact) was placed in the path of the transversely scattered light and it was so orientated as to deviate the rays passing through it in a vertical plane. Immediately behind it was the nicol (transmitting the ultraviolet region also) and further behind another quartz lens which focussed the two images of the track formed by the passage through the double-image prism on the slit of the spectrograph. The slit of the spectrograph was kept rather broad. The two images were well separated, one above the other, crossing the slit and corresponded to vibrations in the scattered light which were initially vertical and horizontal respectively. The spectrograph made use of in the present experiment was a small Hilger quartz spectrograph. In this arrangement the errors arising from the polarisation effects of the spectrograph were automatically eliminated. The nicol in the path of the scattered light was so orientated that the two images

⁵ J. Ramakrishna Rao, *Ind. Jour. Phys.*, 1927, 2, 61; S. Ramachandra Rao, *Ind. Jour. Phys.*, 1928, 3, 1; R. S. Krishnan, *Proc. Ind. Acad. Sci., A*, 1936, 3, 126

of the scattered light for a particular wave-length were of equal intensity. A photograph was taken for this position of the nicol. The nicol was slowly rotated step by step through a degree on either side and a series of photographs was taken for the successive orientations of the nicol. The following six liquids have been investigated thus, *viz.*, benzene, formic acid, acetic acid, propionic acid, normal butyric acid, and isobutyric acid.

3. Results.

In the case of benzene it was found that for one particular orientation of the nicol the two components of the scattered light were of equal intensity for the whole recorded spectrum. With a slight rotation of the nicol either way, the same component (vertical or horizontal as the case may be) became brighter than the other for all the wave-lengths. This clearly shows that benzene does not exhibit any appreciable dispersion of depolarisation. The depolarisation factor ρ_u calculated from the nicol reading for which the two components are equal in intensity is given in Table I.

In the case of formic acid it was found that for a particular orientation of the nicol, the two components were equal in intensity for λ 2536 Å U., whereas the vertical component was still brighter than the horizontal component for λ 4358 Å U. Conversely for another orientation of the nicol when the two components were equal in intensity for λ 4358 Å U, the horizontal component was brighter than the vertical component for λ 2536 Å U. For an intermediate position of the nicol the vertical component for λ 4358 was brighter than the horizontal component, whereas for λ 2536 the horizontal component was brighter than the vertical component. The values of ρ_u for different wave-lengths are given in Table I.

Acetic acid also exhibited a similar phenomenon. In this case it was noticed that when the nicol was so orientated as to equalise in intensity the two components for λ 2536 the horizontal component for λ 4358 was still brighter than the vertical component. Again when the nicol was rotated further so as to equalise in intensity the components for λ 4358 the vertical component for λ 2536 was brighter than the horizontal component. This shows that acetic acid exhibits a dispersion of depolarisation but in the opposite direction. The values of ρ_u for different wave-lengths are given in Table I. In propionic acid also an appreciable dispersion of depolarisation was observed. Normal butyric acid did not transmit the ultra-violet region and exhibited a strong fluorescence in the visible region. Consequently no quantitative measurement of depolarisation was made. Isobutyric acid also strongly absorbed the ultra-violet region. But it did not show any appreciable fluorescence in the visible region.

TABLE I.

λ in A. U.	4358 ρ_u %	4046 ρ_u %	3650 ρ_u %	2967 ρ_u %	2536 ρ_u %
1. Benzene ..	45.5	45.5	45.5	45.5	absorbed
2. Formic acid ..	47	47	49	50.8	52.8
3. Acetic acid ..	44	44	42.2	40.5	36
4. Propionic acid ..	42	42	43.7	44	absorbed
5. Isobutyric acid ..	36	36	36	absorbed	absorbed

4. Theoretical Discussion.

It is well known that the depolarisation factor of the light scattered by the molecules in the gaseous state is a measure of their optical anisotropy, in other words, is due to the fact that the optical polarisabilities of the molecules are different in different directions. K. R. Ramanathan⁶ has derived a formula for the depolarisation of the light scattered transversely by the molecules in the fluid state given by the following expression:—

$$\rho_u = \frac{6\delta}{\frac{5RT\beta n}{N} + 7\delta} \quad \dots \dots \dots (1)$$

where ρ_u = depolarisation factor when the incident light is unpolarised.

R = gas constant

T = absolute temperature.

β = compressibility coefficient.

n and N are the number of molecules per c.c. and per gram molecule of the fluid

δ is what is called the anisotropy factor and it is given by

$$\delta = \frac{A^2 + B^2 + C^2 - AB - BC - CA}{(A + B + C)^2} \quad \dots \dots \dots (2)$$

where A, B and C are the optical moments induced in the molecule when it is placed in a field of unit intensity respectively along its three principal axes. For gases and vapours at low pressures which obey Boyle's law to a

first approximation $\frac{RT\beta n}{N} = 1$ and consequently $\rho_u = \frac{6\delta}{5 + 7\delta} \quad \dots \dots \dots (3)$

⁶ K. R. Ramanathan, *Ind. Jour Phys.*, 1927, 1, 420.

It follows from equations 2 and 3 that if the ratio of the polarisabilities along any two axes in the molecule depends on the wave-length of the incident light wave, the optical anisotropy as well as the depolarisation factor will vary with the wave-length. Such a dispersion of optical anisotropy would be a genuine molecular property. On the other hand, if the ratio of the polarisabilities is independent of wave-length, the depolarisation factor also will be independent of wave-length.

In the case of a non-associated liquid, the depolarisation factor ρ_u is given by the same equation 1 (given above). But the value of δ is given by the following⁷:

$$\delta = \frac{(A' - B')^2 + (B' - C')^2 + (C' - A')^2}{2(A' + B' + C')^2} \quad \dots \quad (4)$$

where $A' = A(1 + p_1 \chi)$

$B' = B(1 + p_2 \chi)$

$C' = C(1 + p_3 \chi)$

p_1 , p_2 and p_3 are the constants of anisotropy of the polarisation field. χ is the susceptibility of the medium. In the case of ordinary liquids also, if the anisotropy factor depends on the wave-length of the incident light wave, the depolarisation factor will show a dispersion. From a comparison of the expressions for ρ_u in the liquid state and in the state of vapour, it is seen that if the molecules in the vapour state do not exhibit any dispersion, no dispersion will be exhibited by them in the liquid state. On the other hand, if they show an appreciable dispersion in the gaseous state they may show a dispersion in the liquid state as well but to a much smaller degree.

The generalisations given above are not applicable to the case of highly associated liquids, such as liquid fatty acids. S. Ramachandra Rao⁸ has studied the variations of intensity and depolarisation factor of the transversely scattered light in the case of a large number of liquids. He finds that in almost all liquids the optical anisotropy as calculated from the depolarisation values increases with rise in temperature. But in acetic acid the anisotropy decreases when the temperature is raised up to 120° C and above that temperature, it increases in the normal way.

Very recently the variations in intensity and depolarisation factor of the transversely scattered light have been studied by the author⁹ in the case of the first four fatty acids with the incident light in the three different states of polarisation, namely unpolarised, horizontally polarised and vertically

⁷ C. V. Raman and K. S. Krishnan, *Phil. Mag.*, 1928, **5**, 498.

⁸ S. Ramachandra Rao, *Indian Journal of Physics*, 1928, **3**, 1.

⁹ R. S. Krishnan, *Proc. Ind. Acad. Sci., A*, 1936, **3**, 126.

polarised. In the case of formic acid and acetic acid the depolarisation factor ρ_h is found to be distinctly less than 1, contrary to the molecular theory of light scattering. ρ_h increases with rise in temperature attaining its limiting value of unity at about 90° C. The intensity of scattering also at first diminishes with rise in temperature in these liquids. These observations have furnished for the first time definite experimental evidence for the existence of large molecular aggregates in these highly associated liquids of size not small compared with the wave-length of light. In these highly associated liquids, the depolarisation factor ρ_u arises not only from the actual anisotropy of the individual scattering particles, but also from their finite size. The depolarisation factor arising from the finite size of the molecular groups will increase with decrease of wave-length. Therefore it is natural to expect an appreciable dispersion of depolarisation. The increase of depolarisation with diminution in wave-length in the case of formic and propionic acids can very easily be explained on the basis of association. In formic acid since the association is greater, the dispersion is also greater than in propionic acid. But it remains unexplained why in the case of acetic acid the depolarisation factor diminishes as the wave-length decreases.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work.

5 Summary

The paper describes the results of measurements on the dispersion of polarisation of light scattered by benzene, formic acid, acetic acid, propionic acid and isobutyric acid. The depolarisation factor for benzene is constant over a wide range of wave-length. In the case of formic acid and propionic acid the depolarisation factor is found to increase and in acetic acid it is found to decrease as we proceed towards the ultra-violet. It is pointed out that the formation of large molecular groups in the fatty acids is probably responsible for the observed dispersion of depolarisation.

ON THE STRUCTURE AND OPTICAL CHARACTERS OF THE NACRE IN IRIDESCENT SHELLS.—PART I.

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1. Introduction

It is common knowledge that the colours exhibited by mother-of-pearl owe their origin to the regularly laminated structure of this substance. The pioneer investigations of Sir David Brewster¹ and the more recent studies of Pfund² and of Lord Rayleigh³ may be cited in this connection. These researches, however, left much ground unexplored. Much has been added to our knowledge of the structure of the nacreous substance by the work of W. J. Schmidt⁴ and his pupils, an account of which is conveniently accessible in the memoir on Bivalves by F. Haas.⁵ On the optical side, the recent work of Sir C. V. Raman⁶ has brought to light a variety of new effects demanding explanation and which have stimulated further investigations into the whole subject.

According to Schmidt, mother-of-pearl consists of microscopically small tablet-shaped crystals of aragonite formed along the basis, the so-called platelets of mother-of-pearl, which are regularly arranged in positions parallel to the surface of the shell and are cemented together by an organic substance, the so-called conchin or conchyolin. The platelets so held together form elementary laminæ and these are in their turn superposed on one another in great numbers and cemented together by extremely thin layers of the same organic substance. The thickness of the elementary laminæ corresponds to that of the platelets of which they are composed, and is of the order of magnitude 1μ but may vary between the extreme

1. For a summary, see his *Treatise on Optics*, 1853, p. 137.

2. A. H. Pfund, *Frankl. Inst. Jour.*, 1917, **183**, 153.

3. Lord Rayleigh, *Proc. Roy. Soc.*, (A), 1923, **102**, 674.

4. W. J. Schmidt, *Die Bausteine des Tierkörpers in Polarisiertem Lichte*, F. Cohen, Bonn, 1924.

5. F. Haas, "*Bronn's Klassen und Ordnungen des Tier-reichs*," Akad. Verlag., Leipzig, 1931, **3**, iii, 1-4.

6. C. V. Raman, *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 567, 574, 859.

limits 0.5μ and 2μ in different species. The actual thickness of the organic layers is exceedingly small compared with that of the aragonite layers and this has been inferred by Schmidt from his observations of the cross-sections of mother-of-pearl under the highest available magnifications. Further, according to Schmidt, mother-of-pearl is an aggregate of crystals, which both in the individual elementary laminæ and also in the neighbouring ones are arranged essentially parallel to one another. This regular arrangement of innumerable single crystals is regarded as explaining the more or less complete optical homogeneity of the substance, indicated by the more or less uniform extinction and axial picture which is determined by the aggregate of the regularly arranged ultimate units. The c axis is normal to the elementary laminæ, and the lines of growth on the shell lie on the axial plane and are parallel to the macro-axis. (In rare cases, the axial plane and the lines of growth cross each other, and the latter then correspond to the brachy-axis.)

'The granular structure of nacre led Raman' to infer that the individual particles in their environment should be capable of diffracting or diffusing light in a manner determined by their size, shape, orientation and grouping relatively to each other in the laminæ. Direct evidence that such diffraction effects do occur is furnished by the diffusion haloes, exhibited by a thin plate of nacre when it is held before the eye and a bright source of light viewed through it. These diffusion haloes form a unique method of revealing the structure of the nacreous substance, and a study of them led Raman to conclude that the structure of nacre is entirely different in the three great divisions of the Mollusca—namely the Lamellibranchs, Gastropods and Cephalopods, and that it also exhibits notable variations as between individual families and species. The Gastropod shells—*Turbo*, *Trochus* and *Halotis* give haloes that form more or less complete circles. That of the Cephalopod—*Nautilus*—is of very peculiar form, consisting of two roughly circular but incomplete arcs of about 60° angle on either side of the direct beam. The bivalve shells, of which five different species were studied by him, give again quite a different type of halo, namely two spots or rather diffraction spectra, one on either side of the central diffraction disc and distinctly separated from it. Closer study reveals that though the diffusion haloes of *Trochus* and of *Halotis* resemble that of *Turbo* in having circular symmetry, they differ strikingly in detail. Similarly, though the different species of bivalves examined show the same general type of diffusion halo, they differ considerably in detail. The size and arrangement of the crystal-line particles in the laminæ can be inferred from the observed character of

7. *Loc. cit.*, pp. 859–860, 865–867.

the haloes as well as their angular dimensions. The haloes observed in the case of *Turbo* and other Gastropods indicate that the crystal particles are arranged in the plane of the laminae without preference for any particular direction, that is with circular symmetry. On the other hand, in the Lamellibranchs, the particles are distinctly smaller in size and are evidently arranged in a manner which stimulates the lines of a coarsely ruled linear grating.

There is a close relationship between the results deduced from the observations of the diffusion haloes and those indicated by a study of the X-ray patterns of mother-of-pearl by Dr S. Rama Swamy,⁸ who examined the nacreous layer of iridescent shells using a monochromatic X-ray beam incident along various directions. From a study of these patterns, it is found that the nacreous layers of all the shells consist of aragonite crystals orientated with their *c* axes normal to the surface. But the orientations of the other two axes vary with the particular kind of shell. The X-ray diffraction patterns for Gastropod shells, like *Turbo*, *Trochus*, etc., with the rays incident normally to the laminations consist of complete circles, while with X-rays incident parallel to them a spot pattern is obtained. These results can be explained by the assumption of crystallites whose *a* and *b* axes are oriented at random, while the *c* axes are normal to the laminations. In the Lamellibranchs such as *Mytilus Viridis* and *Margaritifera Vulgaris* a spot pattern is obtained whether the X-ray beam is incident normally to laminations or parallel to them. This means that the three axes *a*, *b* and *c* exhibit specific orientation with regard to the lines of growth in these shells. In the case of *Nautilus Pompilius* the results of the X-ray analysis indicate an arrangement of twinned crystals, with a specific orientation of the *a* and *b* axes, but with a larger error than in the bivalves.

The present paper describes the results of an investigation undertaken to find whether the structure of the nacreous substance as inferred from the optical haloes and the X-ray patterns is supported by the results of more direct study of thin sections of nacre under the petrological microscope, both with plane polarised light and convergent light.

2 Examination under Plane Polarised Light

Except a few slides which were intended for the study of the diffusion haloes, the others were ground very thin, the average thickness being about 5μ . Apart from a good rub over clean chamois leather the sections were not otherwise polished. In the case of transverse sections and a few others, previous cooking in balsam for about three hours at about 80° – 90° was

8. S. Rama Swamy, *Proc Ind. Acad. Sci., A*, 1934, 1, 871; 1935, 2, 345.

found necessary. The sections were prepared cut in one or another of the three perpendicular directions—namely parallel to the surface of the shell transverse to the surface, and either parallel or perpendicular to the lines of growth on it. Even the optic sections, parallel to the surface, were so cut that the lines of growth could be easily ascertained

For studying the texture and structure of the shells, medium power objectives were generally used, while for measurements of the size of the grains, high power objectives and a micrometer-scale reading to 2μ were used. For the transverse sections and some of the Lamellibranchs, oil immersion objectives (90 X) and oculars of high power (15 X) were found absolutely necessary as the sizes were of the order of 0.4 to 0.5 μ

Lamellibranchata.—The following shells belonging to this family were studied. (1) *Margaritifera Margaritifera*, (2) *Margaritifera Vulgaris*, (3) *Margaritifera Lentiginosa*, (4) *Mytilus Viridis*, and (5) *Lamellidens Marginalis*. These are all fine grained shells, the individual crystals of aragonite being quite small compared to those of the members of the other two families

Under the microscope, they appear very fine-grained (Figs. 5-7), with the crystals of aragonite in tiny platelets of extreme thinness, and all arranged parallel, so that they look like parallel sheafs or bundles of crystals laid linearly one above the other. The crystals are arranged with their vertical axes c all parallel to one another and normal to the lamination plane. The two lateral axes a and b of each crystal are similarly parallel to the corresponding axes of the other crystals and lie in the plane of the optic section. The crystals are all normal and untwinned. On account of the extremely fine size and parallel arrangement, no individual faces are observable in the optic sections, except the a (100) face which appears as fine parallel striations and along which the crystals are bound by a thin layer of conchyolin. It is this structure of the shell that acts like a ruled grating and gives rise to the diffusion halo observed by Raman.

On account of the extreme fineness in size and absence of well-developed faces in the section it is not possible to correctly assess the size of the crystals. But the distance between the striations (Figs. 5-7) gives us the distance between the two a faces which in turn gives us a good idea of the relative size of the crystals in the various shells. The following table gives the size in the various bivalves. The measurements were made by means of a micrometer-scale capable of reading upto 1.6 μ by using high-power objectives and oculars.

<i>Margaritifera Margaritifera</i>	3—4 μ
<i>Margaritifera Vulgaris</i>	2—2.5 μ
<i>Margaritifera Lentiginosa</i>	2.5—3 μ
<i>Mytilus Viridis</i>	1.25—1.5 μ
<i>Lamellidens Marginalis</i>	2—2.5 μ

The crystals, however, are not arranged absolutely parallel. There is a slight tilting of the a plane, sometimes to the right, sometimes to the left, the error in orientation being different in different shells. It is about 4° to 5° in *Margaritifera Vulgaris* and slightly more in *Margaritifera Margaritifera* and *Margaritifera Lentiginosa*. Similarly the disposition of the aragonite crystals, along the different lamination planes also is not absolutely parallel. While there is no change in the direction of the c axes (they are all parallel to one another) there is an error in orientation of the two lateral axes a and b . This is very noticeable if one compares instead of two immediate alternate lamination planes, two which are separated by say about half a dozen. Under crossed nicols, instead of the section becoming completely dark at one position, we get small bright parallel patches here and there, which are extinguished only by turning the section slightly to the right or the left.

In *Mytilus Viridis*, the error in orientation is somewhat large—as much as 15° , not only linearly, but also transversely. It looks as though the two lateral axes are disposed of in an undulating manner, folded as it were. On account of this the optic section, under crossed nicols, presents a curious figure (Figs 11 and 12), with alternate bands of light and shade in both the directions—the characteristic “grating structure” of microcline. In *Lamellidens Marginalis*, the error is slightly less than in *Mytilus Viridis*, but still large enough to indicate a definite tendency for the folding or undulation noticed in the latter. The section, under crossed nicols (Fig 13), looks like a felspar crystal which has developed polysynthetic twinning, only the edges are not so straight and well defined. This is because of not only the error in orientation, but of definite tilting of the lateral axes, now to one side, now to the other.

As is known, the axial plane of aragonite is parallel to a (100) and it is this plane which is observable as series of parallel striations in optic sections under the microscope. On account of the regularity in arrangement of the crystals, there is a definite relationship between this plane and the lines of growth in the shell. In most of the shells it is normal to it, *i.e.*, the lines of growth are parallel to the a axis. In *Margaritifera Margaritifera* it is slightly inclined and in *Margaritifera Vulgaris* the axial plane makes as little as 60° with the lines of growth.

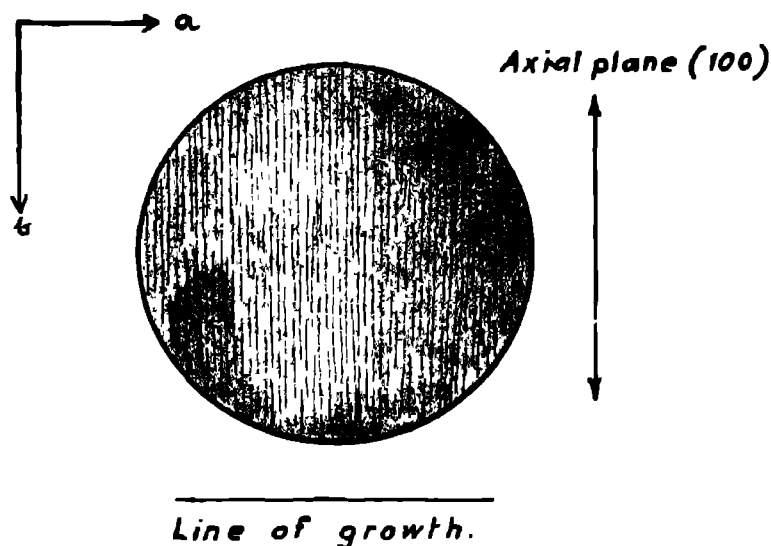


FIG. 1.—To show the orientation of the crystallographic axes and planes in the optic section of a Lamelli branch shell

Gastropoda.—The following shells belonging to this great family were studied: (1) *Turbo* (sp.), (2) *Trochus* (sp.), (3) *Haliotis* (sp.), and (4) *Haliotis* (*Californian Abalone*). These are all coarse grained shells, compared to those of the previous family. Individual crystals of aragonite with well-developed faces are easily discernible under even medium power objectives. The crystals generally are normal, but good many twinned ones are found, the twinning being along the m (110) plane. The twins are the usual doublets, but triplets and multiple parallel series are not absent, though the former is of rare occurrence and the latter rarer still. The size of the crystals covers a wide range. In *Turbo* it is from 4 to 7 μ , in *Trochus* 6 to 12 μ and in *Haliotis* 5 to 8 μ . (In an East African species of the *Haliotis* there seems to be two growths of crystals, one uniform and the other very uneven in size, the latter not being very common but clustered in places.)

The arrangement and disposition of the crystals are not the same as are observed in the members of the Lamellibranchs. The crystals are in thin tiny platelets arranged with their c axes parallel and normal to the elementary laminae. While there is this regular parallelism with regard to the vertical axes of the individual crystals, there is no such orderliness in the disposition of the two lateral axes in these tiny platelets. They are thrown pell-mell with no definiteness in orientation. Under crossed nicols there is no complete extinction at any position (Figs. 14 and 15), different grains getting extinct at different times, the extinction depending upon when their vibration directions happen to coincide with those of the nicols. Thus the optic sections of these shells, under the microscope, look like a

fine grained sandstone, where there is no definiteness in orientation between the various grains of quartz.

Haliotis, Calif. Abalone (III).—Of the three specimens referred to by Raman⁹ in his papers this is the least gorgeous in colour and the top of the nacreous layer is enamel-like. This is also more translucent to light than the others. The crystals generally are untwinned, but twinned ones are not uncommon. Unlike the other Gastropods, there is a tendency here to some arrangement, though not to such an extent as in the Lamellibranchs. Under high power, the optic section (Fig. 8), especially when just thrown out of focus, looks like a bundle of faggots tied together, each faggot representing a bundle of crystals in which the a axes lie along the length of the faggot. As in the other shells the vertical axis is normal to the elementary laminae. The b (100) plane is parallel to the lines of growth.

Cephalopoda.—*Nautilus Pompilius*—This is interesting from many points of view. It is different from the other two families not only in the outer structure of the shell, but also in the structure of its nacreous layer. It is more or less intermediate in its characters. The shell is medium grained, neither so fine grained as the Lamellibranchs nor so coarse as the Gastropods, the size of the crystals ranging from 3 to 6 μ . The crystals are discernible under the medium power objectives, more easily under high powers. Generally the crystals are twinned, though untwinned ones are also observed. Doublets, triplets and quadruplets, in parallel series, are quite common.



FIG. 2.—*Nautilus Pompilius*. Some of the crystal forms observed under the microscope

Under the microscope, when observed with high power, a sort of cross-hatch structure is observed (Fig. 9), the angle between the two sets of line being about 60°. This is due to the twinning of the crystals of aragonite: the twinning plane of aragonite being m (110), so that the angle between two similar faces is 117°. On account of this twinning in regular order and large error in orientation of the crystals there is no complete extinction under crossed nicols. But this is quite different from that observed for the Gastropods. In the latter there is no extinction at all at any time, different grains becoming extinct at different times. But in the case of *Nautilus*, on rotation of the section through a complete range of 360°, we observe

9. *Loc cit*, p. 570.

at four positions maximum illumination and at four other positions, 45° from the previous ones, minimum illumination. This can be explained only on the hypothesis that the arrangement of the crystals is regular, whatever that arrangement may be.

The septum of *Nautilus Pompilius*, which is thin, is also nacreous, but not so iridescent. It is covered by a thin layer of white enamel. In contrast to the main outer shell, the septum is very coarse grained, much coarser than even the Gastropods (Fig. 16). The size of the grains ranges from 12 to 16μ . The crystals are mostly twinned and the arrangement is the same as in the main shell. It is not easy to find out the relationship between the lines of growth and the crystal faces on account of the difficulty of finding out the lines of growth in mounted specimens.

3. Examination under Convergent Light

For further study of the structure of the nacreous layers, the sections were examined under convergent polarised light. The photographs disclose a remarkable variety in the configuration of the interference figures, which disclose the arrangement of the crystals of aragonite in these shells. It will be noticed that the Gastropod shells, *Turbo*, *Trochus* and *Halotis*, give a uni-axial figure, while the Lamellibranchs that of a biaxial figure and the Cephalopod *Nautilus* an intermediate one, a biaxial figure with a small optic axial angle (Plates XXXI and XXXII). This variety in the shape of the interference figures produced can only be explained by considering the arrangement of the individual crystals.

The cause of the interference figures, as we know, is due to the optical anisotropy and consequent double refraction of the crystals belonging to other than the isometric system. In these crystals the velocity of light and hence the refractive index is different in different directions. Rays which enter a biaxial crystal so as to travel through it in any direction other than an optic axis are split up into two rays, vibrating at right angles to each other and with different refractive indices. On account of this difference in the refractive index, a phase difference is introduced in the two rays, travelling in the same direction, and all interference phenomena observed with convergent light is due to this phase difference. The directions of maximum and minimum refractive index lie at right angles to each other and at right angles to these two is a third axis of intermediate refractive index. In uniaxial crystals the intermediate axis coincides with one of the others, so that in planes at right angles to the optic axis the refractive index is the same in every direction. In aragonite, which belongs to the biaxial group, the crystallographic c coincides with the acute bisectrix,

which is the direction of the fast ray. So the platelets of aragonite, we observe in the optic sections, are all perpendicular to the acute bisectrix. If we now consider a number of such platelets of aragonite, all arranged one above the other like the cards in a pack, with their c axes vertical and the a and b axes pointing to definite directions in the horizontal plane, then we obtain a regular biaxial crystal and a corresponding interference figure in convergent light will be obtained. For the regular arrangement leads to a complete optical homogeneity, so that it behaves like a single crystal with refractive index different in different directions. This is what actually happens in the case of Lamellibranch shells.

Let us, however, consider a different arrangement. Suppose the platelets of aragonite are all arranged one above the other with their c axes all vertical, but with their a and b axes pointing not to two specific directions in space but to all possible directions. If we consider any appreciable number of such platelets the resultant will be to destroy any effect of regular orientation in the horizontal plane, so that the combination will become as though it were a uniaxial type cut perpendicular to the optic axis. For the resultant of the various refractive indices of these platelets in any one direction will, for all practical purposes, on account of the random orientation, be the same as the resultant of the various refractive indices of these platelets in any other direction. In other words, the refractive index is the same in every direction in the horizontal plane. So a uniaxial figure is obtained. This is what happens in the case of Gastropod shells where there is no attempt at specific orientation in the horizontal plane.

This can also be explained analytically. It is well known that¹⁰

$$\tan^2 V_f = \frac{\alpha^2 (\gamma^2 - \beta^2)}{\gamma^2 (\beta^2 - \alpha^2)}$$

where V_f = one half the acute optic angle for a negative crystal, in other words it is the angle between one optic axis and the fast vibration direction (a) which is the crystallographic c in aragonite. Now in the Gastropods the effect of complete random orientation of the aragonite platelets is to wipe off the difference between γ and β which in mathematical language might be interpreted as $\gamma = \beta$. Hence in such an arrangement $\gamma^2 - \beta^2$ will vanish so that $\tan^2 V_f$ becomes equal to zero. So V_f is zero that means the optic axes coincide with the acute bisectrix which is equivalent to the crystal being uniaxial. We also see that in these shells, on account

10. A. Johansen, *Manual of Petrographic Methods*, 1914, p. 103

of the definiteness in the orientation of the vertical axis, α remains constant while it is $\gamma - \beta$ that is changing. Since α is constant

$$\tan^2 V_f \text{ varies as } \gamma^2 - \beta^2.$$

In *Nautilus* due to twinning and also to a large error in orientation the effective difference between γ and β is reduced, though not cancelled, so that $\gamma - \beta$ is a small quantity. Hence $\tan^2 V_f$ becomes small; in other words a biaxial interference figure with a small axial angle is obtained.

Margaritifera.—As explained already, the arrangement of the individual crystals of aragonite is very regular in the three *Margaritifera* species examined and consequently the interference figure observed is a biaxial one (Figs 17–19). Even here among the three species there is a slight difference in that the error of orientation is not the same, the error being large in *M. Margaritifera* and small in *M. Vulgaris*. This can also be inferred from a study of the interference figures. The optic axial angle observed in *M. Vulgaris* is the greatest while it is the least in *M. Margaritifera*.

Mytilus Viridis.—Here also there is a regularity of orientation as in the *Margaritifera*. Consequently the interference figure is a biaxial one (Fig. 20). But as already mentioned the arrangement here is not so perfect as in the previous shells. Due to the folding or tilting of the lateral axes, as we move the section along the lines of growth or at right angles to it, the interference figure, instead of remaining steady, as it should be

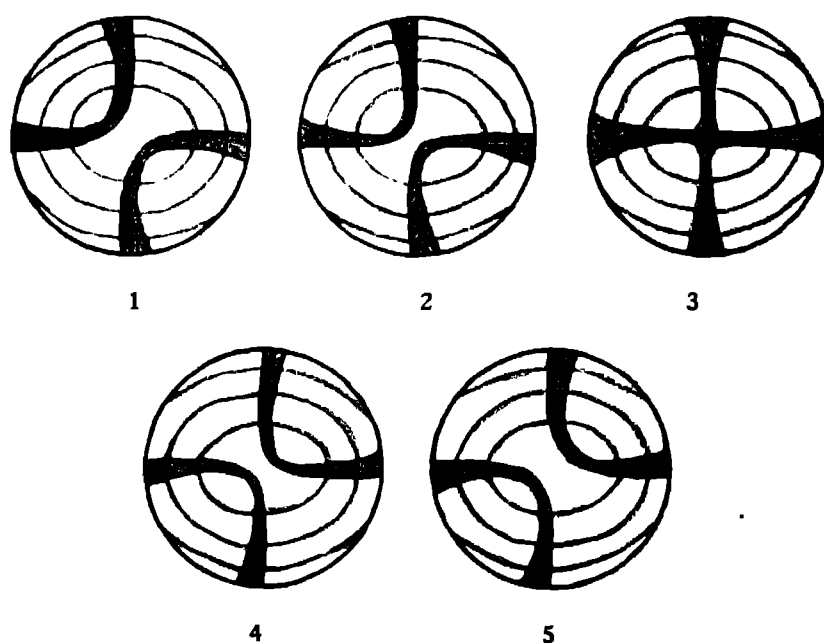


FIG. 3—Interference figures of *Mytilus Viridis*, showing the tilt in the Axial Plane when the section is moved along the lines of growth.

if there were optical homogeneity, jumps hither and thither, while there is a change in the optic axial plane as shown by the series of figures below, with also a change in the axial angle. This change in the optic axial plane and axial angle, as the section is moved under the microscope, either along the lines of growth or perpendicular to it, cannot be accounted for except by the tilt or folding in the axes and the consequent error in orientation

Lamellidens Marginalis (Fig 21).—This also behaves very much similar to the previous shell. There is jump in the axial figure and also a change in the axial angle. Only, it is not so pronounced as in *Mytilus Viridis*. This is quite in keeping with the observations made under plane polarised light

Gastropods.—All the shells belonging to this family gave under convergent light a uniaxial figure. *Turbo*, *Trochus* and *Halotis* (Figs 22–24). This is, as has already been explained, due to the random orientation of the platelets of aragonite

Halotis, Calif Abalone —There is a tendency for a biaxial figure with a small axial angle (Fig 25). As we rotate the stage, the isogyres come and meet and then part, though on a small scale. This is because there is a tendency here in this shell, for a rough parallel grouping and not such random orientation as in the other Gastropods

Nautilus Pompilius.—This gives a biaxial figure with a small axial angle (Fig 26). The smallness of the axial angle is due to the twinning and large error in orientation of the crystals in the different laminae

All the photographs of the interference figures were taken in monochromatic light, the source being a mercury arc with green filter

4 Diffusion Haloes

Raman¹¹ has fully explained the phenomena of the diffusion haloes observed when thin sections of the nacre are held against a bright source of light and viewed through. As explained before, nacre is composed of very thin parallel laminae cemented together, each of which consists of a great many individual crystalline particles arranged in some kind of order. These individual particles diffract and diffuse light in a manner depending on their size, shape, orientation and grouping relative to one another in the laminae. We may refer here, by way of analogy to a paper by Prins¹² who has given photographs showing how the diffraction haloes due to a group of particles varies with their arrangement. With lycopodium powder

¹¹ Loc cit

¹² v. J. A. Prins, *Doe Natuurw*, 1931, 19, 435

dusted on a glass plate in such manner that the grains are very loosely and irregularly distributed, we obtain a corona with a bright central disk surrounded by alternate bright and dark rings. This pattern is progressively modified as the grains are more closely packed together, tending to a more uniform distribution. The central disk becomes less and less in intensity, until ultimately, when the grains are quite evenly and tightly packed, the corona disappears and is replaced by a diffusion halo which is separated from the image of the source of light by a dark region. The size of the halo depends on the size of the grains and wave-length of the light employed.

It has already been shown how the shape, orientation and grouping of the individual crystals observed in various nacreous shells agree generally with the conclusions arrived at by Raman by the study of the diffusion haloes. It is possible to calculate the size of the grains from the haloes assuming the nacre to form an irregular type of grating and applying the usual diffraction formula

$$d \sin \theta = n\lambda$$

where d is the size of the grain which determines the distance between the successive diffracting centres

The sections cut for the present work were thicker, about $20-30\mu$ than were used for the microscopic work. Further, both the sides were polished with the finest rouge on chamois leather, and then mounted on a slide with canada balsam and cover slip. For the source of light a mercury arc was used and the green filter for the production of monochromatic light. The lens of the camera was removed and in its place the section covered with a thin metal disc with a pin hole pierced through. By means of a suitable condenser a parallel beam of light was allowed to fall normally on the metal disc. Before photographing it was necessary to carefully orientate the specimen held in the lens panel till the complete halo was obtained on the ground glass screen, for unless the laminæ are normal to the rays the full halo is not obtained.

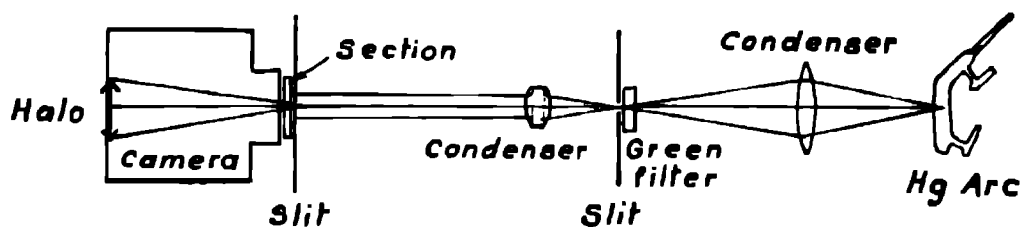


FIG. 4—Arrangement of the Apparatus for photographing the Diffusion haloes.

			Size as calculated from the Diffusion Halo	Size actually measured under the microscope
			μ	μ
<i>Margaritifera Margaritifera</i>	3.2	3 to 4
<i>Margaritifera Vulgaris</i>	2.2	2 to 2.5
<i>Margaritifera Lentiginosa</i>	2.6	2.5 to 3
<i>Mytilus Viridis</i>	1.25 to 1.5
<i>Lamellidens Marginalis</i>	2.3	2 to 2.5
<i>Turbo</i> (sp.)	5.3	4 to 6
<i>Trochus</i>	6 to 12
<i>Haliotis</i> (sp.)	5.6	5 to 8
<i>Haliotis Calif. Abalone</i>	5.6	5 to 8
<i>Nautilus Pompilius</i>	4.8	3 to 6

In the table above is given the size of the grains as calculated from the diffusion haloes as well as the size actually measured with the micrometer scale under the microscope. It will readily be seen that the two figures are of the same order of magnitude. Further, it was noticed that the disparity in the size of the grains had a bearing on the sharpness of the haloes, where the difference was great, the haloes were diffuse and where it was small they were sharp.

The thickness of the lamination planes and a study of the transverse sections, light absorption, etc., will form the subject of another paper.

In conclusion I wish to express my sincere thanks to Sir C. V. Raman for suggesting the above investigation and for the constant interest he took during the course of the work, and also for placing at my disposal his rich collection of beautiful shells. My thanks are also due to Dr. S. Rama Swamy for the help rendered during the preparation of this paper.

5. Summary.

This paper deals with the microscopic study of the texture and structure of the nacre of iridescent shells. These were examined under plane polarised light as also under convergent light, and measurements were made of

OPTIC SECTIONS UNDER PLANE POLARISED LIGHT

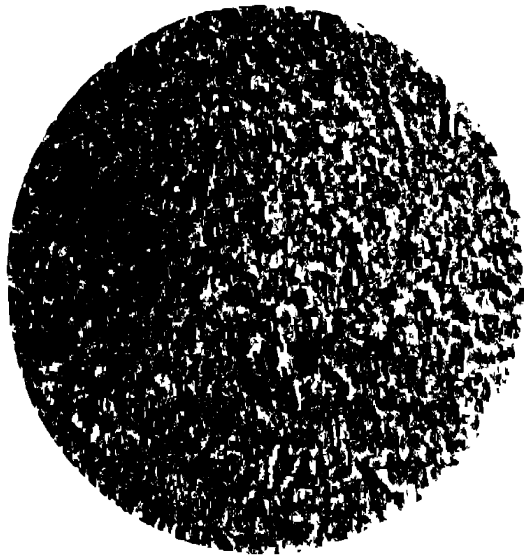


FIG 5 *Margaritifera Margaritifera*

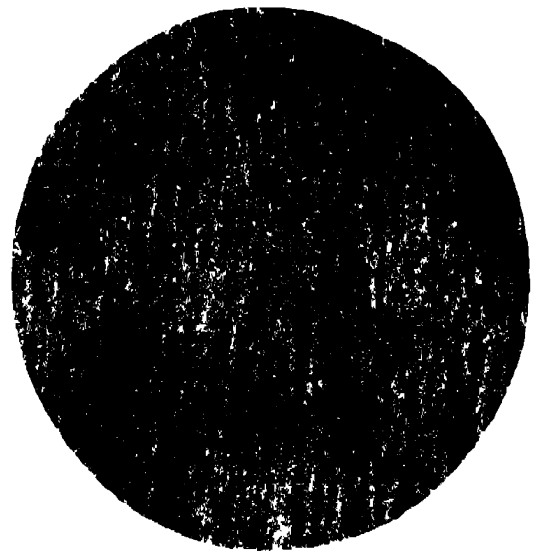


FIG 6 *Margaritifera Vulgaris*

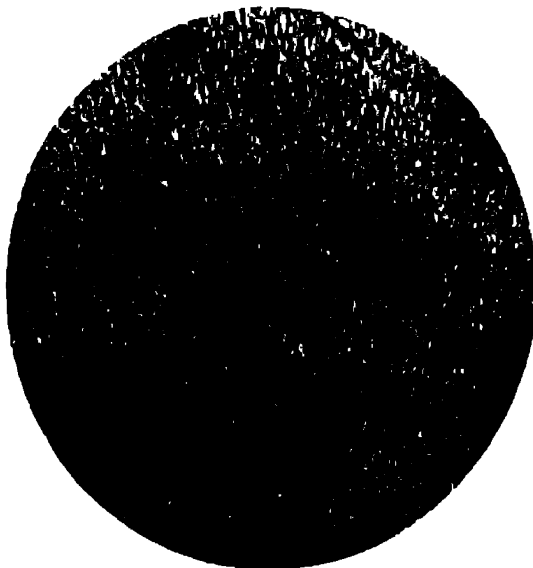


FIG 7 *Mytilus Vindes*

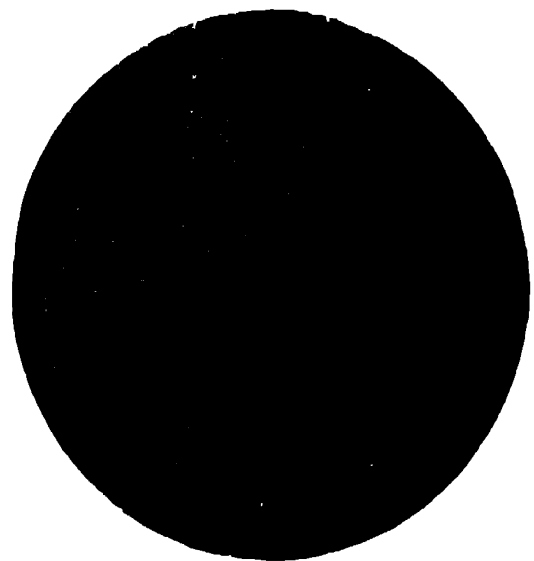


FIG. 8 *Halotis (Californian Abalone)*

OPTIC SECTIONS UNDER PLANE POLARISED LIGHT

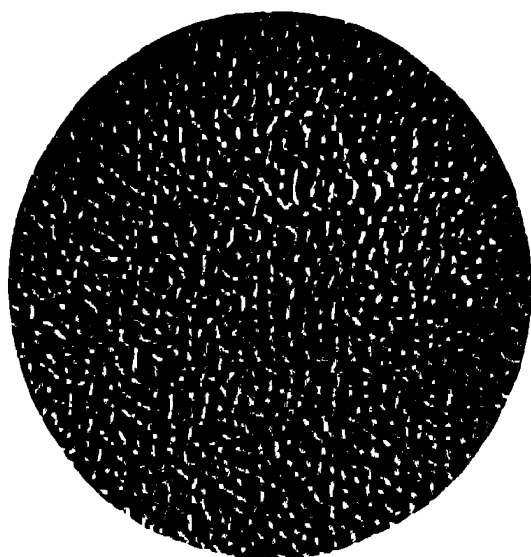


FIG. 9 *Nautilus Pompilius*

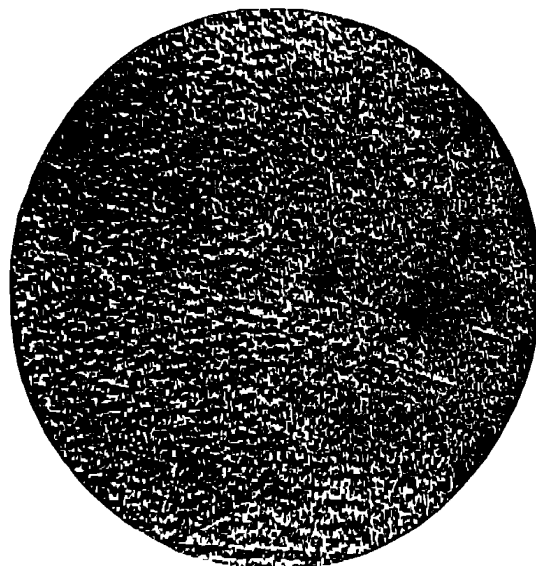


FIG. 10 Septum of *Nautilus Pompilius*.



FIG. 11 *Mytilus Fendius*
(under crossed nicols)



FIG. 12 *Mytilus Fendius* (thicker than 11)
(under crossed nicols)

OPTIC SECTIONS UNDER PLANE POLARISED LIGHT



FIG. 13 *L. undulatus Magnatilis*
(under crossed nicols)

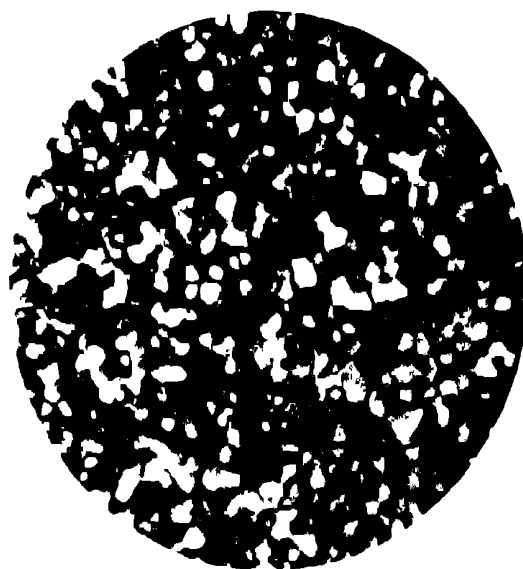


FIG. 14 *Trochus* (sp.)
(under crossed nicols)

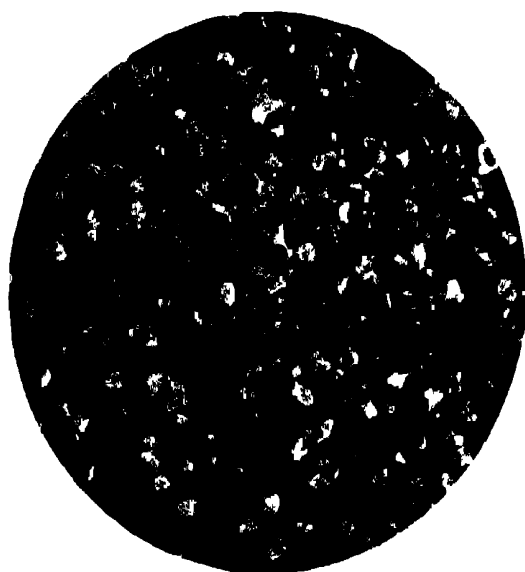


FIG. 15 *Halotis* (sp.)
(under crossed nicols)



FIG. 16 Septum of *Vautalus*,
(under crossed nicols)

OPTIC SECTIONS UNDER CONVERGENT LIGHT.
(INTERFERENCE FIGURES)

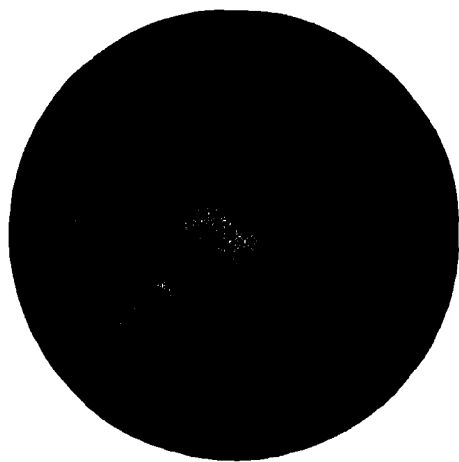


FIG. 17 *Margaritifera Margaritifera*

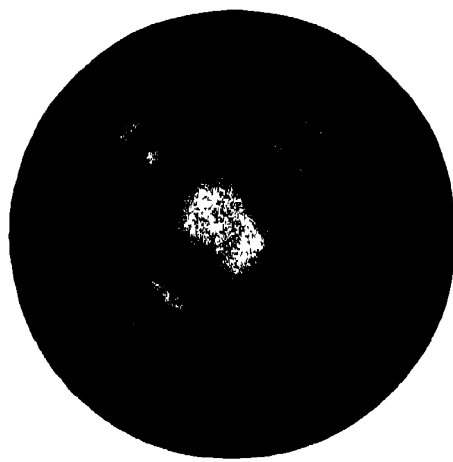


FIG. 18 *Margaritifera Vulgaris*

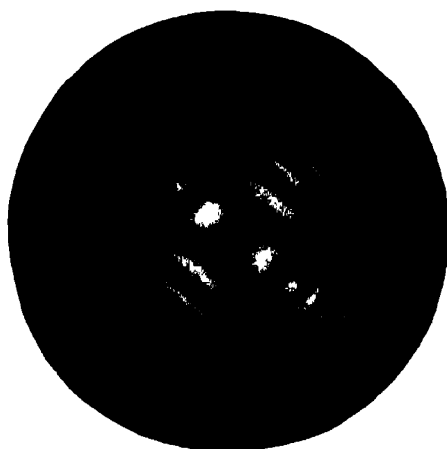


FIG. 19 *Margaritifera Lenticulosa*

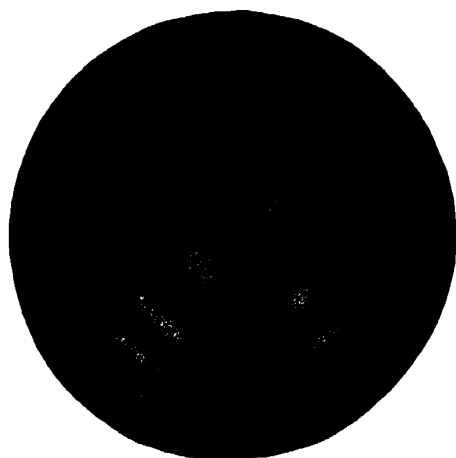


FIG. 20 *Mytilus Fordii*

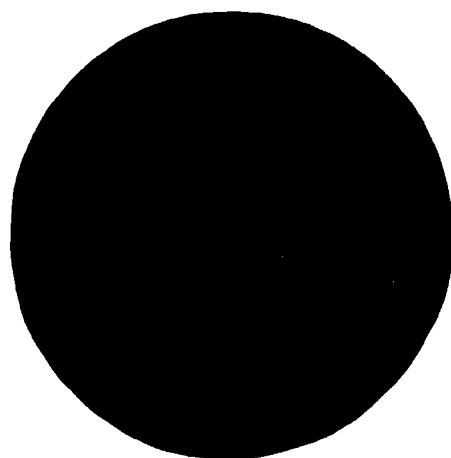


FIG. 21 *Lamellidens Marginalis*

OPTIC SECTIONS UNDER CONVERGENT LIGHT.
(INTERFERENCE FIGURES)

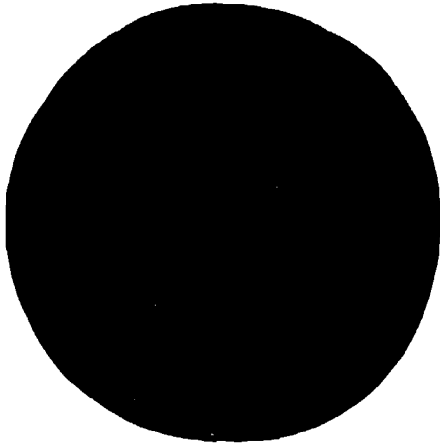


FIG 22 *Turbo* (sp.)

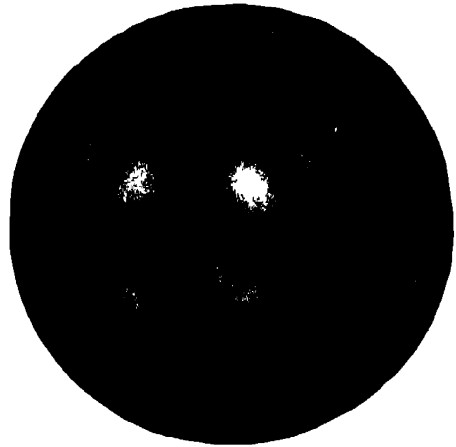


FIG 23 *Trochus* (sp.)

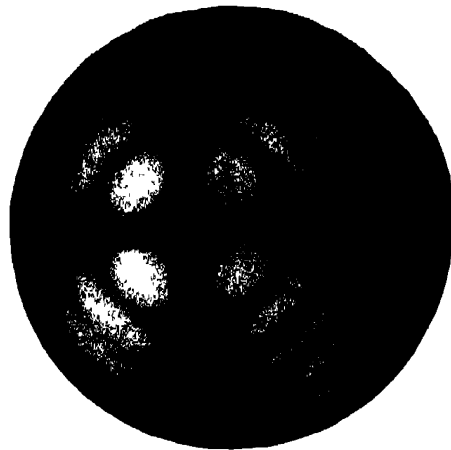


FIG. 24, *Halotis* (sp.)

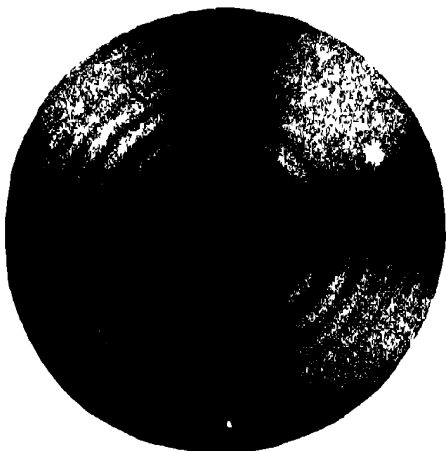


FIG 25 *Halotis* (Californian Abalone.)

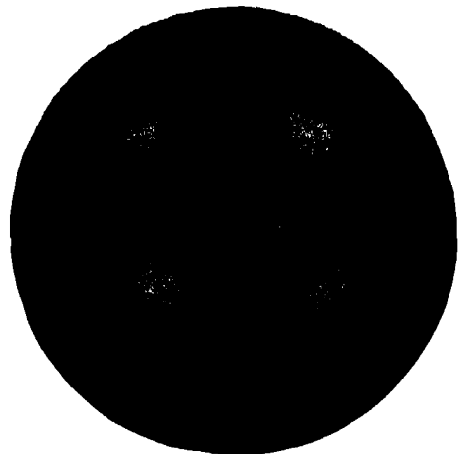


FIG. 20. *Nautilus Pompilius.*

the size of the grains under the microscope and compared with those calculated from the diffusion haloes with which they were in satisfactory agreement. The crystals of aragonite, which form the nacre in these shells, are very fine in the Lamellibranchs, medium sized in the Cephalopods and coarse in the Gastropods. Further the crystals in the Lamellibranchs are all normal and no trace of twinning is found. In the Gastropods both normal and twinned crystals are found while in the Cephalopod *Nautilus* twinned ones are the general rule. It is also found that in all these shells the aragonite crystals are in tiny platelets of extreme thinness, regularly arranged in positions parallel to the surface of the shell and held together by an extremely small quantity of cementing medium of an organic substance—the so-called conchyolin. These tiny platelets are orientated with their vertical axes c normal to the surface of the shell. But the orientation of the two other axes varies with the particular kind of shell examined, depending generally on the family to which it belongs. In the Lamellibranchs, where the crystals are the most orderly in arrangement, the two lateral axes are oriented in definite directions and with definite bearing to the lines of growth on the shell. In the Gastropods the crystals are randomly oriented, *i.e.*, the two lateral axes point not to two specific directions in the shell, as in the Lamellibranchs, but to all possible directions. *Nautilus* occupies an intermediate position in that the $a b$ plane of the crystals has a specific orientation but with a large error. On account of this variation in the arrangement of the crystals in the three different families of the Molluscan shells the interference figure, observed with thin sections under convergent light, is also different. The Lamellibranchs give a biaxial figure, the Gastropods a uniaxial figure, while the Cephalopod *Nautilus*, which occupies an intermediate position, a biaxial figure with a small axial angle. The size of the grains as measured under the microscope is in close agreement with that calculated from the diffusion haloes. The results obtained by the microscopic examination of thin sections closely correspond with the optical observations of Sir C. V. Raman and those indicated by a study of the X-ray patterns by Dr. S. Rama Swamy.

THE PHYSICAL IDENTITY OF ENANTIOMERS. PART II.*

(a) The Rotatory Dispersion of *d*-*l*- & *dl*-forms of
Iso-nitrosocamphor and their Sodium Derivatives.

(b) The Differences in the Physiological Action of *d*-, *l*- &
dl-forms of Sodioisonitrosocamphor.

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AND

SHRONATH PRASAD.

(From the Chemical Laboratories, Science College, Patna)

Received May 22, 1936

IN the present communication we record the optical rotatory dispersion of iso-nitrosocamphors (*d* and *l*) in three solvents and of their sodium derivatives in water. An account of the experiments on the physiological action of the sodioisonitrosocamphors (*d*, *l* and *dl*) is also given

Forster¹ found that two isomeric benzoyl derivatives of iso-nitrosocamphor, one yellow and another white, are formed when iso-nitrosocamphor is acted upon by benzoyl chloride in presence of sodium hydroxide. The yellow benzoyl derivative when hydrolysed by alcoholic potassium hydroxide gave colourless needles (m.p. 152–153° C) from boiling light petroleum. Attempts to hydrolyse the colourless derivative resulted in the formation of α -camphor nitrilic acid. Later Forster² succeeded in getting the other isomeride of iso-nitrosocamphor melting at 114° C from the yellow *m*-nitrobenzoyl iso-nitrosocamphor.

Still more recently a convenient method of separating the two isomerides of iso-nitrosocamphor has also been described by Forster.³ He separates them by fractional precipitation of the isomerides from their aqueous solution of sodium salts by acetic acid.

Patterson and his collaborators⁴ have studied the rotatory dispersion of isonitroso-*d*-camphor (stable variety). In 2.5 per cent. alcoholic solution,

* This work was carried out at Ravenshaw College, Cuttack.

¹ *J. C. S.*, 1903, **83**, 526

² *Ibid.*, 1904, **85**, 904

³ *Ibid.*, 1926, 2671.

⁴ *Ibid.*, 1932, 1715

their results can be represented by the general simple dispersion equation, namely,

$$[\alpha]_{\lambda}^{25^{\circ}} = \frac{52.4}{\lambda^2 - 0.0857} \quad (\lambda = 1358 \text{ to } 6716).$$

We have studied the rotatory dispersion of both the stable and unstable isomerides of iso-nitrosocamphors (*d* and *l*) and of the sodium derivatives of the stable forms. Our results agree with the one-term formula. The value of rotation constant (*k*) is higher for the stable than for the unstable form.

The racemic variety of isonitrosocamphor as well as the *laevo*-form are new substances. Whereas in the case of the *laevo*-isomer both the stable (m p 152° C) and the unstable (m p 114° C) isomers have been isolated, only one form (m p 108° C) of the racemic variety could be obtained. As this was obtained by melting the crude product which was precipitated by 20 % acetic acid from the aqueous solution of iso-nitrosocamphor (*dl*), we believe it is the stable form. The unstable form is an oil which refused to solidify.

The physical identity of the *dextro*- and the *laevo*-forms of iso-nitrosocamphor and of their sodium salts is also established, as is evident from the tables of rotatory dispersion (Tables I to VII).

Relation between physiological action and stereoisomerism—The above-mentioned equality in magnitude of the rotatory dispersion of the enantiomerides is no longer observed in their biological action. It is well known that optically active antimers have different action on living matter: thus *l*-nicotine, when injected into the blood of an animal produces pain, excitation and finally death; *d*-nicotine, on the other hand, causes only a strong temporary shivering when similarly injected. With the object of studying the physiological action of *d*-, *l*- and *dl*-forms of camphor and its derivatives, one of us prepared and forwarded several of these isomers in three forms to Colonel R. N. Chopra, I M S, Director, Tropical School of Medicine, Calcutta. As these compounds were insoluble in water, their solutions in alcohol, glycerol and olive oil were investigated. Control experiments with the pure solvents alone showed varying degree of pharmacological effects. It was thus clear that the water insoluble isomers were not suitable for this study. The sodio derivatives of *d*-, *l*- and *dl*-iso-nitrosocamphor are soluble in water and lend themselves admirably for this work. These compounds are readily soluble in normal saline and yield clear pale yellow solutions. Colonel Chopra's report on the effect of these isomers on the blood pressure, heart *in situ* and the isolated heart is discussed below. With the sodio-derivative of *d*-isonitrosocamphor, the blood pressure is reduced, the effect being rapid

but temporary in nature. The heart beats are slowed but the muscular tone is increased in isolated heart when perfused with dilutions of 1 in 500,000 to 1 in 1,000,000. The coronary circulation is reduced. With the *lævo*-variety, under the same conditions, the fall in blood pressure is less marked, whereas in the case of *dl*-form, the effect is nil.

The rabbit's heart was stimulated with 1 in 1,000,000 dilution of the *dextro*-compound, but it was soon followed by depression, slowing of the rhythm and later on followed by irregularity of contractions. The *lævo*-variety produced only a mild stimulation with 1 in 50,000 to 1 in 100,000 dilutions, whereas under these conditions, the effect of the racemic form was nil.

When 10 milligrams of the *dextro*-compound was injected in cat intravenously, there was a fall of blood pressure. The blood pressure gradually returned to normal. This effect was practically absent in the *l*- and *dl*-isomers. The pulse rate was reduced from 200 to 160 beats per minute with the *dextro*-compound, whereas the *l*- and *dl*-forms did not produce such a marked effect.

In the case of frog's heart the action was much delayed. There appeared to be a slight stimulation when 0.1 c.c. of 1 per cent. solution of the *dextro*-compound was injected intrahepatically. The stimulation was more marked, though much delayed in occurrence. After about 10 minutes, a periodicity was noticed and there was a block in the conduction of impulses through the bundle. These effects disappeared after washing the heart with fresh saline. The *l*- and *dl*-isomers did not produce any marked effects.

The above-mentioned physiological experiments have some significance on the nature of the racemic form in solution. If the racemic form is an equimolecular mixture of the *dextro*- and *lævo*-forms, its physiological effect should be intermediate between the *dextro*- and *lævo*-forms. The evidence so far adduced shows that the physiological effects of the racemic form of the sodioisonitrosocamphor are much less marked than those of the *dextro*-compound and in some cases they are even milder than those of the *lævo*-form. It may be, therefore, inferred that racemic form of sodioisonitrosocamphor is not a mixture but a compound of the *d*- and *l*-forms. The physiological action of the *dextro*-form of sodioisonitrosocamphor is much greater than that of the *lævo*-form.

Experimental.

Sodium beads (8.5 g) were immersed in dry ether (250 c.c.) in a flask, fitted with a condenser and a drying tube, and surrounded by melting ice. Camphor (54 g) was added in small quantities and when completely

dissolved was treated in dim light with redistilled amyl nitrite (45 g.) added in small amounts. After the first few additions, the liquid became yellow. Any tendency to froth was checked by agitation and control of temperature. Subsequently the added quota was increased and the rest of the amyl nitrite was added. The reddish brown product was left in ice in a semi-dark place for 1 to 2 hours. A small quantity of solid substance appeared afterwards. In semi-darkness, ice and water were added until a reddish brown aqueous layer separated from the pale yellow ethereal solution. It is to be recalled that sodium derivative of the unstable isomeride when dissolved in water and exposed to light is transformed into the stable modification.

After removal of the aqueous layer the ethereal portion was twice washed with water. The aqueous layer was again extracted twice with small quantities of ether to remove borneol and unchanged camphor, being finally freed from ether by blowing a current of air. Dilute acetic acid (20%) was constantly added to the alkaline fluid at 0° C. in small quantities and often shaken till the volume of added acetic acid became 72 c.c. The faintly yellow precipitate was washed with ice water and ice-cold dilute acetic acid and again with ice water. Dried in air this product weighed 5 grams (m.p. 112–113° C.). The filtrate which is still yellow was transferred to a beaker and on further addition of acetic acid to it, white precipitate was thrown down (m.p. 135° C.). The precipitate (15 g.) was dried, melted and acetic acid (20%) added to it. On repeated crystallisation from acetic acid, needle-shaped white crystals (9.5 g.) were obtained (m.p. 152° C.).

The melting was done at 135° C. though Forster advises to melt the crystals at 152° C. The yield is quite good even if the crystals are melted at 135° C. and then crystallised out of 20% acetic acid.

l-iso-nitrosocamphor was prepared in the same manner from *l*-camphor obtained by oxidising *l*-borneol with chlorine water. The stable iso-nitrosocamphor gave m.p. 152° C., while unstable form gave m.p. 114° C.

Found: C = 65.7; H = 8.5; $C_{10}H_{16}NO_2$ requires C = 66.3 per cent; H = 8.28 per cent.

Preparation of sodio-derivative of stable variety of iso-nitrosocamphor (d and l)—5 g. of iso-nitrosocamphor was treated with 5 g. of sodium hydroxide in 20 c.c. water. A yellow solution resulted. The solution was concentrated on water bath. On cooling yellow crystals of sodio-derivative of iso-nitrosocamphor separated which were filtered and washed with small quantities of water, followed by ether. The yield was 4 grams.

Found: Na, 11.1, $C_{10}H_{14}O_2N Na$ requires Na = 11.31 per cent.

The yellow salt is hygroscopic, insoluble in ether and benzene and sparingly soluble in alcohol. It is extremely soluble in water and in aqueous solution reacts alkaline to litmus. Cobalt nitrate solution in water gives buff-coloured characteristic precipitate with aqueous solution of the salt, while ferrous sulphate solution gives green and nickel chloride solution white precipitate.

The racemic iso-nitrosocamphor (m.p. 108°C) was prepared in the same manner from racemic camphor.

Found: C = 66.65; H = 7.67; $\text{C}_{10}\text{H}_{15}\text{NO}_2$ requires C = 66.3 per cent; H = 8.29 per cent.

The sodium derivative was prepared in the same way as that of the *dextro*- and *laevo*-isomeride.

The rotatory power determinations were made in a 2-dm jacketed tube at 35°C . The value of λ_0 calculated from the dispersion formula is given in the tables and is expressed as μ or 10^{-4}cm .

TABLE I.

Iso-nitrosocamphor (stable) in Benzene.

$$[\alpha] = \frac{45.56}{\lambda^2 - 0.0921}; \lambda_0 = 0.3035$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Laevo</i>		
Concentration g./100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
1.0021	+ 1.00°	+ 128.3°	Li_{6709}	127.3°	- 129.1°	+ 1.80°	1.0165
"	+ 1.20	163.7	Li_{6104}	162.5	161.2	- 1.30	"
"	± 0.00	178.7	Na_{5893}	178.7	180.8	+ 2.10	"
"	- 1.20	187.6	Hg_{5750}	188.8	188.7	- 0.10	"
"	- 2.20	219.0	Ag_{5469}	221.2	220.1	- 1.20	"
"	± 0.00	221.1	Hg_{5461}	221.1	219.4	- 1.70	"
"	- 1.60	272.0	Cd_{5085}	273.6	274.1	+ 0.50	"

TABLE II.

Iso-nitrosocamphor (stable) in Ethyl Alcohol

$$[\alpha] = \frac{53.74}{\lambda^2 - 0.0740}; \lambda_0 = 0.2720$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Laevo</i>		
Concentration g./100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
1.001	- 2.7°	+ 140.3°	Li ₆₇₀₉	143.0°	- 143.0°	± 0.0°	1.014
"	- 0.5	157.4	Cd ₆₄₃₈	157.9	156.1	- 1.8	"
"	- 0.3	179.7	Li ₆₁₀₄	180.0	180.5	+ 0.5	"
"	- 1.5	195.2	Na ₅₈₀₃	196.7	197.2	+ 1.5	"
"	- 2.0	204.6	Hg ₅₇₈₀	206.6	206.0	- 0.6	"
"	+ 1.2	241.2	Hg ₅₄₆₁	239.8	239.8	± 0.0	"
"	- 0.6	290.5	Cd ₅₀₈₅	291.1	293.0	+ 1.0	"

TABLE III.

Iso-nitrosocamphor (stable) in Chloroform.

$$[\alpha] = \frac{49.41}{\lambda^2 - 0.0875}, \lambda_0 = 0.2958$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Laevo</i>		
Concentration g./100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
1.1015	- 0.1°	+ 136.2°	Li ₆₇₀₉	136.3°	- 134.0°	- 2.3°	1.2015
"	± 0.0	151.1	Cd ₆₄₃₈	151.1	153.0	+ 1.9	"
"	+ 1.2	174.6	Li ₆₁₀₄	173.4	175.0	+ 1.6	"
"	- 1.3	189.0	Na ₅₈₀₃	190.3	188.1	- 2.2	"
"	+ 1.7	203.2	Hg ₅₇₈₀	201.5	204.2	+ 2.7	"
"	+ 1.2	235.8	Hg ₅₄₆₁	234.6	235.5	+ 0.9	"
"	± 0.0	268.8	Ag ₅₂₀₉	268.8	268.0	- 0.8	"
"	+ 0.3	289.1	Cd ₅₀₈₅	288.8	288.7	- 0.1	"

The solution exhibited muta-rotation, the initial value $[\alpha]_{\text{Hg}_{5461}} = 235.8^\circ$ and $[\alpha]_{\text{Hg}_{5780}} = 203.2^\circ$ changing to 258.9° and 233.6° respectively in the course of 69 hours.

TABLE IV.

Iso-nitrosocamphor (unstable) in Benzene.

$$[\alpha] = \frac{34.76}{\lambda^2 - 0.1143}; \lambda_0 = 0.3380$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Laevo</i>		
Concentration g./100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
1.4816	-1.46°	+102.10°	Li ₀₇₀₀	103.56°	-103.00°	-0.56°	1.4915
"	+0.50	116.30	Cd ₀₄₃₈	115.80	116.00	+0.20	"
"	-1.40	133.20	Li ₀₁₀₄	134.60	136.00	+1.40	"
"	+0.04	150.24	Na ₅₈₀₃	149.30	150.00	+0.70	"
"	-0.86	157.40	Hg ₅₇₈₀	158.26	157.82	-0.40	"
"	-1.56	188.24	Hg ₅₄₆₁	189.80	190.56	+0.77	"
"	+0.55	221.75	Ag ₅₂₀₀	221.20	222.11	+0.91	"
"	-0.80	240.10	Cd ₅₀₈₅	240.90	242.15	+1.25	"

TABLE V.

Iso-nitrosocamphor (unstable) in Ethyl Alcohol.

$$[\alpha] = \frac{34.70}{\lambda^2 - 0.1385}; \lambda_0 = 0.3721$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Laevo</i>		
Concentration g./100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
1.3916	+0.50°	+109.20°	Li ₀₇₀₀	108.70°	-108.29°	-0.41°	1.3915
"	-0.79	123.01	Cd ₀₄₃₈	123.80	124.26	+0.46	"
"	+0.20	146.20	Li ₀₁₀₄	146.00	146.50	+0.50	"
"	-0.50	167.10	Na ₅₈₀₃	167.60	167.01	-0.59	"
"	+0.02	176.02	Hg ₅₇₈₀	176.00	175.48	-0.52	"
"	+0.08	214.38	Hg ₅₄₆₁	214.30	214.30	±0.00	"
"	-1.10	256.20	Ag ₅₂₀₀	257.30	257.01	-0.29	"
"	-0.59	284.01	Cd ₅₀₈₅	284.60	284.97	-0.37	"

TABLE VI.

Iso-nitrosocamphor (unstable) in Chloroform

$$[\alpha] = \frac{41.24}{\lambda^2 - 0.1044}; \quad \lambda_0 = 0.3231$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Levo</i>		
Concentration g/100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g/100 c.c.
1.5032	+ 0.60°	+ 120.00°	Li ₆₇₀₉	119.40°	- 118.85°	- 0.55°	1.5122
"	- 0.50	132.50	Cd ₆₄₃₈	133.00	132.80	- 0.20	"
"	- 0.80	153.00	Li ₆₁₀₄	153.80	154.50	+ 0.70	"
"	+ 0.04	170.00	Na ₅₈₀₃	169.96	169.12	- 0.84	"
"	+ 0.04	180.00	Hg ₅₇₈₀	179.60	180.00	+ 0.40	"
"	+ 0.05	213.00	Hg ₅₄₆₁	212.95	213.10	+ 0.15	"
"	+ 1.50	248.50	Ag ₅₂₀₉	247.00	246.15	- 0.85	"
"	- 0.55	266.85	Cd ₅₀₈₅	267.40	267.84	+ 0.44	"

TABLE VII.

Sodium derivative of iso-nitrosocamphor in Water (prepared from stable iso-nitrosocamphor).

$$[\alpha] = \frac{28.7}{\lambda^2 - 0.1636}, \quad \lambda_0 = 0.4044$$

<i>Dextro</i>			Line λ	Calc. $[\alpha]$ = c	<i>Levo</i>		
Concentration g/100 c.c.	$\sigma - c$	Obs. $[\alpha]$ = σ			Obs. $[\alpha]$ = σ'	$\sigma' - c$	Concentration g./100 c.c.
0.435	+ 0.40°	+ 98.80°	Li ₆₇₀₉	98.4°	- 98.0°	- 0.4°	0.503
"	± 0.00	112.30	Cd ₆₄₃₈	112.3	113.1	+ 0.8	"
"	+ 0.10	134.90	Li ₆₁₀₄	134.8	135.6	+ 0.8	"
"	- 0.90	152.50	Na ₅₈₀₃	153.4	151.0	- 2.3	"
"	+ 0.30	165.60	Hg ₅₇₈₀	165.3	164.9	- 0.4	"
"	- 1.00	208.00	Hg ₅₄₆₁	209.0	209.6	- 0.3	"
"	- 0.50	261.00	Ag ₅₂₀₉	261.5	262.5	+ 1.0	"
"	+ 0.30	296.00	Cd ₅₀₈₅	296.5	295.8	- 0.7	"

No mutarotation.

DIFFRACTION OF LIGHT BY ULTRASONIC WAVES—PART II.*

Reflection and Transmission Phenomena.

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1 Introduction

WHEN Lucas and Biquard, and Debye and Sears discovered at about the same time, the diffraction of light by high frequency sound waves various theories were proposed to account for the phenomenon by Debye and Sears,¹ by Brillouin², by Lucas and Biquard³ and very recently by Raman and Nath⁴ Raman and Nath's theory accounts very satisfactorily for the distribution of intensities in the various orders of spectra and is in good agreement with the earlier and the more recent experimental results of R. Bar⁵ Their theory considers the amplitude and phase changes occurring in the transmitted beam, which will eventually give for the beam of light, after transmission through the medium, a corrugated wave front This gives rise to various orders of diffraction spectra with intensities given by their formula It also brings out quite clearly the dependence of the intensity of the various orders, on the supersonic amplitude, wave-length of light and the length of the acoustic field through which the light traverses

But the earlier theory of Brillouin, quite different in the treatment, explained the diffraction of light by supersonic waves in liquids as due to reflection of light from striations in the medium due to the sound waves. The success of Raman-Nath's theory has put Brillouin's theory somewhat in the background But the possibility of such reflection of light by high frequency sound waves cannot be overlooked when one is dealing with sound of very small wave-length, although we know from the work of Lord Rayleigh⁶ that the intensity of such reflection of light by a liquid of varying refractive index is so small as almost to be overlooked. But under suitable conditions of experimentation, it is possible to detect this reflection Experiments

* Part I is the paper with the same title published in the *Proc. Ind. Acad. Sci.*, 1936, 3, 442.

carried out in this direction have proved conclusively that reflection of light does occur when the sound wave-length in the liquid is very small, quite apart from transmission occurring in all cases. This paper gives a proof of the existence of Brillouin reflections from sound waves of very high frequency travelling in liquids.

2. *Experimental.*

In an earlier paper,⁷ we described the arrangement for a detailed study of the relationship between the angle of inclination of the quartz oscillator and the asymmetry in the diffraction spectra. We follow here the same notations with regard to the (+) and (−) orders and the same method of procedure.

The Fig. 1 of that paper holds good here also. Pronounced asymmetry is observed with greater orders on the (+) side when the quartz is turned through an angle as indicated by the arrow in the diagram.

As we expect this reflection to occur when the wave-length of sound in the medium is very small, the frequency of oscillation was increased to 20×10^6 c/s. This would give roughly a wave-length of 0.065 mm. for a liquid having the velocity of sound about 1300 m./s. This proved very satisfactory.

The steel pointer attached to the holder of the quartz oscillator, measured from rotation axis to the tip of the pointer exactly 333 mm., and a displacement, therefore, of the end of the pointer through 1 mm. on a vertical scale kept at the end, gave an angle of $10' 18''$. At times, whenever it was found necessary, the pointer was turned through even half a millimetre, so that any effect desired, such as the appearance or disappearance of any particular wave-length could be realised.

The liquids employed were toluene and butyl bromide. For the frequencies employed, these liquids gave sound wave-lengths of 0.0651 mm. and 0.0501 mm. respectively. The latter liquid was especially good for this work, as even the dispersion between two successive orders of spectra was greater.

With the quartz plate set at different inclinations to the incident beam, photographs of the spectra were taken on Ilford panchromatic plates. It was thought desirable to register all the wave-lengths of light of mercury arc, from 3650 \AA to 5770 \AA ; as then the photograph will reveal the changes accompanying each wave-length of light employed at various inclinations. This proved in the end quite satisfactory, revealing many features.

Results of observations are given in the next section.

3. Results.

Figs 1, 2 and 3 give the complete results obtained at 20 Mc for the respective inclinations of the quartz, given on one side of the figure. Fig. 1 gives the diffraction spectra in butyl bromide for a position corresponding to the maximum intensity in the first order. Fig. 2 contains the diffraction spectra in toluene for which the sound wave-length is 0.0651 mm, while Fig. 3 is for butyl bromide, the corresponding sound wave-length being 0.0501 mm. We shall now give the results, figure by figure.

For brevity, we shall represent the prominent mercury lines 3650 Å, 4046 Å, 4358 Å, 5461 Å and 5770 Å by the letters *a*, *b*, *c*, *d* and *e* respectively. This is also the notation used in the figures.

Case (a).—Butyl bromide (Fig. 1):

Observations were first made with butyl bromide, since the separation between the orders is great. Visual examination of the diffraction spectra with respect to the position of maximum intensity in the first order for 4358 Å was carried out. After careful adjustment, a photograph of the diffraction spectrum was taken, for which 4358 Å of the first order (+) was at its maximum intensity as seen visually. The two photographs in Fig. 1 relate to the two positions of the quartz oscillator, namely,

(1) when it is parallel to the beam of light, and

(2) when it is at an inclination for which the intensity of 4358 Å of the first order was a maximum. The readings were noted.

Inclination 0°.—The diffraction spectrum is symmetrical; *a*, *b*, *c*, *d* and *e* of the first order and *a*, *b*, *c* of the second order but very much less intense, are recorded.

Inclination 15' 27".—This was the position for which 4358 Å line of the (+) 1 order was most intense. While generally *a*, *b*, *c*, *d* and *e* of the first order on the (+) side have greatly increased in intensity (more than twice) the same lines of the same order on the (−) side have greatly diminished in intensity. The photograph shows it remarkably enough. The second order (+) *a*, *b*, *c* have only slightly increased compared with those in 0° position, while the corresponding lines on the (−) side are completely absent. The second order *d* and *e* lines have also come out very feebly. The photograph is interesting in that the (+) first order is very intense in comparison with (−) first order, which has very nearly disappeared.

Case (b).—Toluene (Fig. 2):

Inclination 0°.—The photograph for 0° gives a symmetrical pattern of the diffraction spectrum, the wave-lengths *a*, *b*, *c*, *d* and *e* being very prominent. The second order for the first three lines shows very feebly.

Inclination 10' 18":—At 10' 18" inclination of the quartz, the second order on one side (+) for the *a*, *b*, *c* lines is bright. It is observed that the first order for these *a*, *b*, *c*, *d* and *e* lines are much brighter on the (+) side than the corresponding lines on the (−) side.

Inclination 20' 36":—For this inclination of the quartz oscillator, the intensity is a maximum for *a*, *b* and *c* lines of the second order (+), while *d* of the same order is visible. The mercury line *e* for second order has made an appearance. It can be very well noticed that the first order *a*, *b*, *c* lines on the (+) side have fallen in their intensity compared with those for inclination 10' 18". This position of the inclination is unique in that the mercury lines 3650, 4046 and 4358 Å of the second order are at their maximum intensity only just here. Since these lines are close together, it is difficult to say very clearly for which one of these three, this position gives maximum intensity. We shall, therefore, take them together.

Inclination 30' 54":—Strangely, while the first order (+) spectrum for the lines *a*, *b*, *c*, *d* and *e* diminished in intensity for 20' 36" position, the same lines for this position have strengthened, but are nonetheless less intense than those for 0° position. This is significant, for *a* and *b* of the second order have almost vanished, while *c* of the same order is only weak. The second order spectrum for *d* and *e* lines are very prominent and are at their maximum intensity here. The third order spectra for *b* and *c* have also appeared but are weaker than the corresponding lines in the second order spectrum.

Inclination 41' 12":—For this position, all the higher order spectra have completely vanished, while even the first order spectrum for the lines *a*, *b*, *c*, *d* and *e* are weak. Those on the (−) side are definitely much weaker than the ones on the (+) side.

Case (c) —Butyl bromide (Fig. 3).

Inclination 0°:—The diffraction spectrum is symmetrical. The first order lines are prominent, while the second order *a*, *b*, *c* are weak.

Inclination 10' 18" —The first order (+) spectral lines are in greater strength than those on the (−) side, while *a*, *b*, *c* of the second order (+) are very prominent.

Inclination 26' 15".—The second order *d* (+) is prominent. The *a*, *b*, *c* of the second order (+) are each of equal intensity. This remark is pertinent as the next para will show, where it is observed that the intensity of one is much less than the other two. (The time of exposure for this picture was much less, due to some cause)

Inclination 30' 54".—The *a* line of the second order (+) has weakened very much compared with *b* and *c* which are strong. The *d* and *e* of the same order are fairly strong. The first order (+) for all lines are correspondingly more intense than those on the (−) side. It would appear that this is the position of maximum intensity for 4358 Å (second order +).

Inclination 36' 3".—Even the *b* and *c* of the second order (+) have weakened enormously while the *a* line has disappeared. The spectral lines *d* and *e* of this order are at their maximum intensity. This position corresponds to that of greatest intensity for 5461 Å (+, second order).

Inclination 46' 21".—All the second order spectral lines have vanished altogether for this position, leaving the first order, both + and −, weak.

In all the above three cases, (*a*), (*b*) and (*c*), more orders appear on that side most favourable for reflection. A reference to a similar situation can be made to the author's paper in the *Proceedings of the Indian Academy of Sciences*, Vol. III, page 442, wherein Fig. 1 exactly depicts by arrow the direction of rotation of the quartz and the part of the spectrum marked (+) where more orders are seen.

We shall discuss the significance of these results in the next section.

In addition to the results mentioned above, relating to the photographs of the spectra at different inclinations of the quartz crystal to the incident light beam, a number of visual observations were also made relating to the progressive changes in intensity accompanying the inclination of the quartz. It is thought, however, useful to give the changes in intensity for only 5461 Å (which is more sensitive to the eye than others) at various angles recorded above for both toluene and butyl bromide. The intensities given in numbers are as viewed by the author visually and though, not exact determinations, they show the changes in intensity.

Case (a) —The relative intensities for case (*a*) are not given, for the photograph very strikingly shows the difference in intensities between the (+) and (−) first orders. While the (+) 1 order has more than doubled in intensity, the (−) 1 order has greatly weakened to probably 1/10th its value for parallel incidence of light.

Case (b) —The table below gives relative intensities made visually for 5461 Å when toluene was used.

TABLE I.

*Relative Intensities for different Orders of Spectra for 5461 Å only
(In Toluene.)*

Inclination of Quartz in minutes of arc	- Order		+ Order	
	2	1	1	2
0°	..	5	5	0
10' 18"	..	4	10	1
20' 36"	..	2	10	2
30' 54"	..	1	6	3
41' 12"	..	$\frac{1}{2}$	3	0

maximum

Case (c).—Below are given visual estimates of intensities for different orders of spectra

TABLE II

*Relative Intensities for different Orders of Spectra for 5461 Å only
(In Butyl Bromide)*

Inclination of Quartz in minutes of arc	- Order		+ Order	
	2	1	1	2
0°	..	5	5	0
10' 18"	..	4	10	1
26' 15"	..	3	8	3
30' 54"	..	3	8	5
36' 3"	..	3	6	6
46' 21"	..	2	4	0

maximum

4. Discussion

It is well known from the work of Bragg that in the case of reflection of X-rays by layers of similar atoms, the reflection obeys the law

$$m\lambda = 2d \sin \theta$$

where m is the order of the diffraction spectrum ;

λ is the wave-length of X-rays ;

d is the spacing distance ;

and θ is the angle between the incident beam and the surface (*i.e.*, 90° —angle of incidence).

Brillouin arrives at a similar formula for reflection occurring from sound wave fronts in a liquid, as modified by

$$m\lambda = 2 \lambda^* \sin \theta$$

where λ^* is the wave-length of sound,

and λ is the wave-length of light employed.

We can verify the existence of pure reflection of light by high frequency sound waves by varying the parameters occurring in the above formula. In addition, where reflection occurs on tilting the quartz plate, the reflected beam moves through twice the angle of incidence. This affords a further verification.

The foregoing section contains results of experiments carried out in this direction. We shall now discuss the results with reference to each parameter, taking the three cases individually.

Case (a).—Butyl bromide (Fig. 1):—Since almost the entire intensity of the first order is concentrated on the (+) side for a glancing angle of $15' 27''$, we shall consider only this case, omitting the second order, the intensity of which has not very much increased compared with 0° position. Brillouin's reflection formula requires for 4358 \AA (the maximum intensity for which the crystal was rotated through) and for the wave-length of sound 0.00501 cm. , a glancing angle of $14' 55''$ for the first order. We obtained experimentally for this position an angle of $15' 27''$, calculated from a displacement of 1.5 mm. of the end of a pointer 333 mm. long. This is in good agreement with the theoretical angle of $14' 55''$ for reflection.

Further, we can calculate the angle between the reflected beam and the transmitted beam (which is, say r), which must equal twice the angle through which the quartz has been rotated (say twice i). We measure the distance d between the zero order and the first order 4358 \AA line as also the distance from the centre of the camera lens to the photographic plate. The respective measurements give 8.413 mm. and 958 mm. which give for the reflected beam an angle equal to $30' 20''$. The glancing angle as given above is $15' 27''$, double of which is $30' 54'' (= 2i)$. This is very near to $30' 20'' (= r)$ of the reflected beam. This confirms the above remark that much light is reflected by ultrasonic waves into the first order at this inclination.

Case (b) :—Toluene (Fig. 2) :—Though the first order (+) is more intense than the (−) order for 10' 18", we shall consider only the second order reflections, as we can easily follow the intensity changes in *a*, *b*, *c*, *d* and *e* for this order.

Second order spectrum : (a) for wave-length 4358 Å :—

For this wave-length of light and for the sound wave-length of 0.00651 cm employed, the second order reflection angle is 22' 57". The maximum of intensity for this line (along with 3650 Å and 4046 Å) was found to occur at 20' 36".

(b) for wave-length 5461 Å : The theoretically calculated angles occur at 28' 47" for 5461 Å and at 30' 24" for 5770 Å, while experimentally the greatest intensity for these lines was found at 30' 52". The agreement in these cases is satisfactory.

Third order reflection :—The third order reflection was observed for only two lines, namely *b* and *c*. The theoretical glancing angles are 31' 57" and 34' 26" while at 30' 54" both were noticed. This is quite possible in view of the nearness of the angles to each other, and the reflection angle not being unique.

The following table gives a comparison between theory and experiment for reflection angles in toluene for the particular sound wave-length employed.

TABLE III

Reflection Angles (for 2nd and 3rd Orders of Spectra) for Sound Wave-length of 0.0651 mm (In Toluene.)

Wave-length of light		Reflection angle in minutes of arc		Displacement of the pointer in mm at a length of 333 mm.	
Symbol	in Å U.	Theoretical	Experimental	Theoretical	Experimental
<i>For 2nd orders</i>					
<i>a</i>	3650	19' 13"	20' 36"	1.87	2.0
<i>b</i>	4046	21' 18"	20' 36"	2.07	2.0
<i>c</i>	4358	22' 57"	20' 36"	2.23	2.0
<i>d</i>	5461	28' 47"	30' 54"	2.80	3.0
<i>e</i>	5770	30' 24"	30' 54"	2.95	3.0
<i>For 3rd orders</i>					
<i>b</i>	4046	31' 57"	30' 54"	3.10	3.0
<i>c</i>	4358	34' 26"	30' 54"	3.34	3.0

Angle of the reflected spectrum.—For 4358 Å and for second order, the angle r as defined above = 45' 20" while i read off from the inclination of the quartz is 20' 36" which is very nearly half r ; similarly for 5461 Å, the angle r for two orders of reflection = 57' 4" and this is very nearly double the angle i = 30' 54", the position of maximum reflection for second order 5461 Å realised experimentally. Considering the conditions of experimentation, the agreement is satisfactory and proves the existence of second order Brillouin reflection.

Case (c) —Butyl bromide (Fig 3).

First order Brillouin reflection has been considered separately under Case (a) and we shall mainly confine our attention to second order reflection.

Second order spectrum.—for wave-length 4358 Å :—The second order reflection for 4358 Å was found to occur in the experiments at 30' 54" and the theoretical reflection angle is 29' 50"

For wave-length 5461 Å :—Experimentally it was found that at a glancing angle of 36' 3", the reflection maximum for second order 5461 Å occurred. The theoretically expected angle is 37' 20" which does not differ by much from the angle 36' 3". The agreement for both the wave-lengths is good.

TABLE IV

*Reflection Angles for Two Orders for Sound Wave-length of 0.0501 mm.
(In Butyl Bromide.)*

Wave-length of light		Reflection angle in minutes of arc		Displacement of the pointer in mm. at a length of 333 mm.	
Symbol	in Å U	Theoretical	Experimental	Theoretical	Experimental
<i>a</i>	3650	24' 59"	25' 45"	2.43	2.5
<i>b</i>	4046	27' 42"	..	2.69	..
<i>c</i>	4358	29' 50"	30' 54"	2.90	3.0
<i>d</i>	5461	37' 20"	36' 3"	3.63	3.5
<i>e</i>	5770	39' 30"	..	3.84	..

Angle of the reflected spectrum :—The calculations regarding r and i are repeated for butyl bromide for the second order for the wave-lengths 4358 Å and 5461 Å. The reflected beam for the second order 4358 was found to make an angle of 60' 40" (= r) with the parallel incident beam, while the

quartz plate was rotated through $30' 54'' (= i)$ which is very nearly half the above angle r . For 5461 \AA , the two angles are as given below, for the second order reflection: $r = 75' 20''$; $i = 36' 3''$ both determined experimentally. The agreement between theory and experiment is satisfactory.

Furthermore, we know very well that when a beam of light is reflected by layers of sound waves, as in these experiments, the angle θ , at which reflection is a maximum for a particular wave-length of light (λ), is uniquely determined for a given wave-length of sound (λ^*). The formula $m\lambda = 2\lambda^* \sin \theta$ gives us further information that the smaller the λ^* , the greater is the

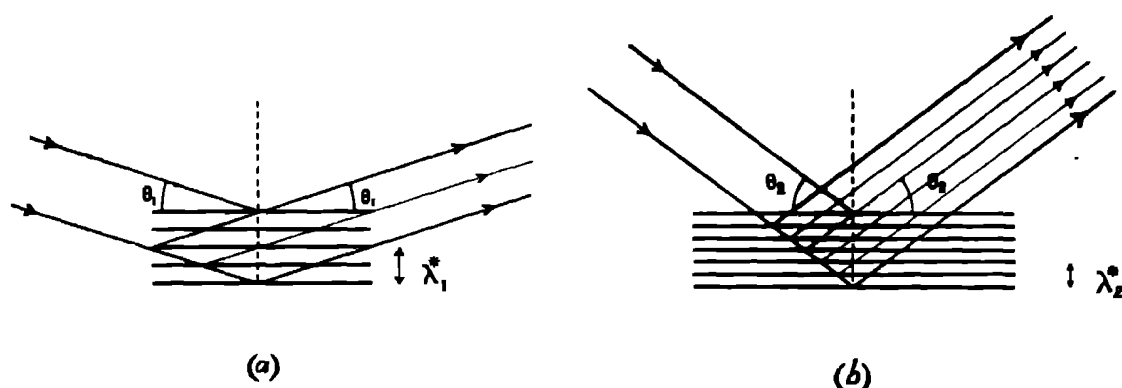


FIG. 4.

angle θ at which reflection occurs. Fig 4 expresses diagrammatically the whole relation, $m\lambda = 2\lambda^* \sin \theta$ for the same values of m and λ in both cases pictured under (a) and (b). The thick horizontal lines indicate sound wave-fronts in the liquid, the distance between any two being half the wave-length of sound, and the oblique thinner lines indicate the path of ray. The glancing angles are θ_1 for (a), and θ_2 for (b). For smaller λ^*_2 as in (b), θ_2 is greater than θ_1 .

That this is so has also been verified experimentally, which again indicates that the phenomenon is due to reflection of light by high-frequency sound waves. The table below gives the glancing angles for the quartz for second order reflection.

TABLE V.

Wave-length of light	Wave-length of sound	θ (Experimental)
5461 \AA	0.00651 cm	30' 54"
" "	0.00501 "	36' 3"
4358 \AA	0.00651 "	20' 36"
" "	0.00501 "	30' 54"

Intensities of the reflected light for different orders :—We have observed in all the cases cited above that the reflection occurred successively at the first, second and third order and at no higher. For even a small rotation of the quartz above the third order reflection angle, the entire diffraction spectra completely disappeared leaving only a faint first order. It was observed in all these experiments that generally the first order reflection spectrum was most intense, the second order less and the third order feeble. We shall make a comparison of their intensities in one particular case.

Since the time of exposure was the same for all the photographs, all other conditions remaining identical, it is possible to make a comparison of intensities for various orders of reflection. The intensities of 4046 and of 4358 for any one spectrum are comparable and we give below the relative intensities for 4358 only at different inclinations where reflections of various orders occur.

TABLE VI
Relative Intensities for 4358 Line of Different Orders of Reflection

Order of the spectrum and nature of the phenomenon	Intensity
1st order Transmission ..	10
1st order Transmission and Reflection ..	20 to 25
2nd order Reflection ..	8
3rd order Reflection ..	2

These quantitative results definitely indicate that Brillouin reflection does occur at very small wave-lengths of sound in the liquid.

It may be remarked here that S. M. Rytov⁸ has made some observations on these phenomena but no photographs of reflection have been reproduced. Further, his paper was published at a time when the nature of the entire phenomenon of diffraction was not well understood, and much before the Raman-Nath theory appeared.

It is necessary to state here that the existence of reflection of light by ultrasonic waves does not create any difficulties in the Raman-Nath theory of diffraction. We have to recognise these two sets of phenomena, reflection and transmission, when we deal with the question of diffraction of light

by ultrasonic waves, and each is a distinct entity by itself. The reflection is very prominent at high frequencies, of the order of 20×10^6 c/s, while it is almost negligible or very little at 1 or 2 megacycles, so that transmission is the predominant phenomenon at the latter frequency. We must regard both of them to exist together, and the exact ratio of preponderance of one over the other will be determined solely by the wave-length of sound in the liquid; whether it is small of the order of 0.07 mm. or less, or 0.2 mm. and greater. As examples, we shall take Fig. 1, which shows (+) 1 order very bright, while (–) 1 order has almost vanished. Probably the ratio of intensities of (+) 1 to (–) 1 will show how much is due to reflection and how much due to transmission phenomena. On the other hand, Fig. 2 in the author's earlier paper⁷ shows that probably reflection takes place up to the position marked 22', while the diffraction spectra suggest that the major phenomenon occurring is transmission. A complete theory ought, therefore, to take into account both reflection and transmission of light, with a function of the wave-length of sound and of light together, which will take proper care of these phenomena.

Here we may remark that from the identical nature of the formula connecting λ and λ^* derived from different standpoints by Raman and Nath from transmission, and by Brillouin from reflection, one gets further support to conclude that the nature of the diffraction is essentially a combination of both phenomena occurring together to different extents, depending on the ratio between λ and λ^* .

The author is highly grateful to Sir C. V. Raman, Kt., F.R.S., N.L., for his interest in the work.

Summary.

With sound of wave-lengths 0.0651 and 0.0501 mm. in liquid, light is found to get reflected in accordance with Brillouin's formula $m\lambda = 2\lambda^* \sin \theta$. The formula is satisfied with different values for m , λ and λ^* . Further, confirmation is obtained by the verification of the relation between the incident and the reflected angles, when the reflected beam moves through twice the angle of rotation of the reflecting surface. Photographs of reflection of the first, second and third orders for some prominent mercury lines are reproduced. It is made out clearly that transmission (Raman-Nath's theory) and reflection (Brillouin's theory) are two separate phenomena, superposed on each other, in the case of diffraction of light by high-frequency sound waves. Remarkably enough, the treatment for diffraction by both the methods leads to the same formula, which enhances the difficulty of separating out the intensities due to each cause.

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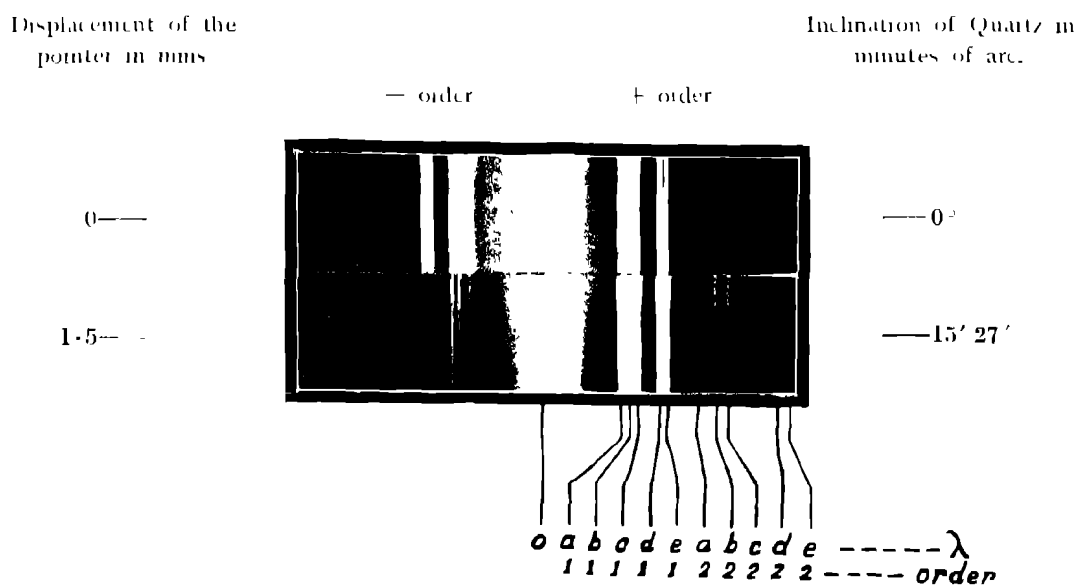


FIG. 1

Diffraction Spectra in Butyl bromide at 20 Mc

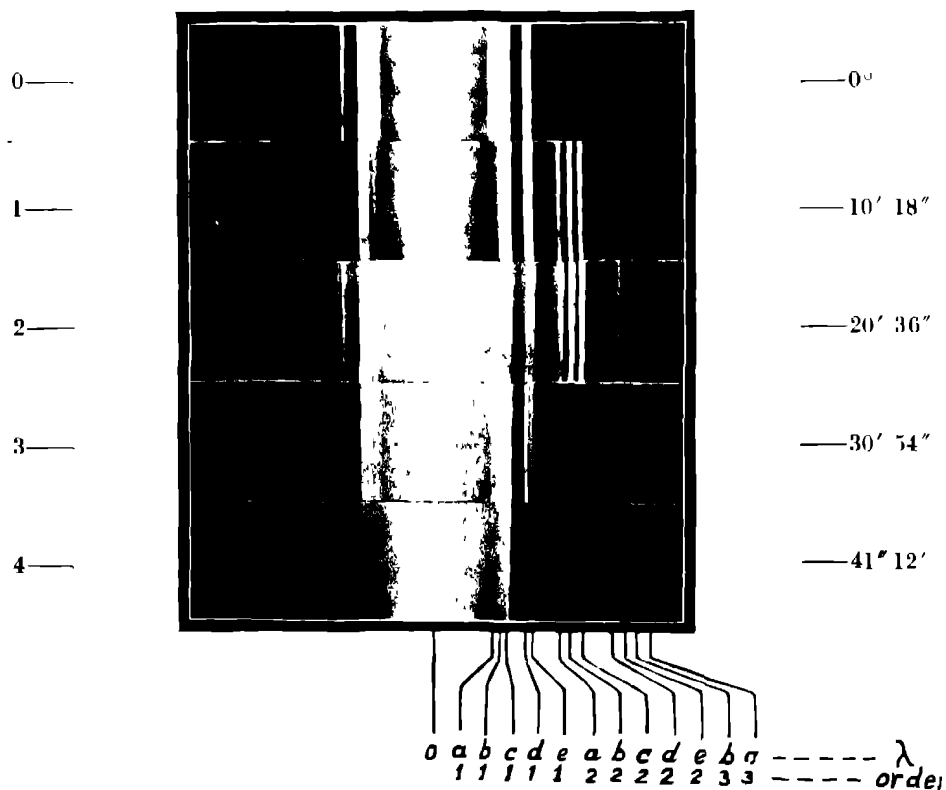


FIG. 2.

Diffraction Spectra in Toluene at 20 Mc.

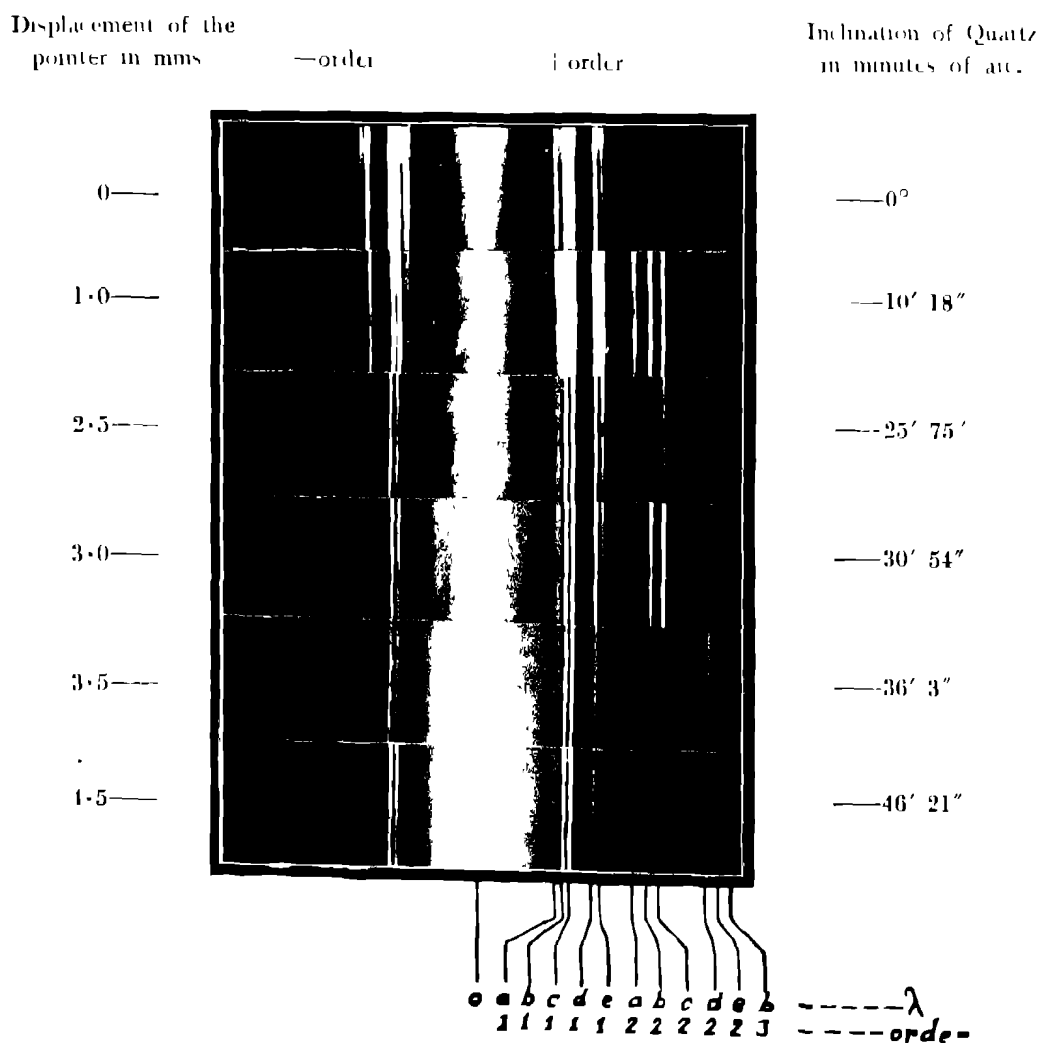


FIG. 3

Diffraction Spectra in Butyl bromide at 20 Mc.

In Figs. 1, 2 and 3, the letters represent the wave-lengths of light
a for 3650Å, *b* for 4046Å, *c* for 4358 Å, *d* for 5461 Å
 and *e* for 5770Å

DOPPLER EFFECT IN LIGHT SCATTERING IN LIQUIDS.

Part III. Polarisation of Light Transversely Scattered by Formic and Acetic Acids.

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(Communicated by Sir C. V. Raman, Kt, FRS, NL)

A previous communication¹ by the author described observations on the state of polarisation of the spectral components of monochromatic light transversely scattered by liquids. The scattered light was examined with the aid of the Fabry-Perot etalon in conjunction with a Fuess spectrograph and some rather surprising results were obtained. It was found that while the two Brillouin (Doppler) components were completely polarised as is to be expected theoretically, the central undisplaced line was also apparently completely polarised. In all the three liquids examined (carbon tetrachloride, toluene and carbon disulphide), no rings whatever could be distinguished on the continuous background when the Fabry-Perot pattern was photographed through the Nicol with its plane of vibration axis perpendicular to the position in which the rings are seen most clearly. This appeared at first sight very surprising in view of the fact that the polarisation of the total unresolved scattered light observed transversely is imperfect to the extent of 46% in toluene and 62% in the case of carbon disulphide. This apparent paradox is resolved if we assume that the depolarised part of the scattered light appears only in the continuous spectrum or wings on either side of the Rayleigh line and that the central undisplaced component arises from individual molecules capable of free rotation. The latter assumption would give us a central undisplaced component which is almost completely polarised even in the case of highly anisotropic molecules. Considering the case of carbon disulphide for example, the light scattered by individual molecules should show a depolarisation of the order of only 11% but if the molecules are free to rotate the depolarised part would mostly appear in the P and R branches and only a small part of it in the Q branch. The Q branch in the light scattered by liquids would thus, unless

¹ B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1935, 2, 236.

the molecules are highly anisotropic and are restricted from rotating, be more or less completely polarised. These considerations indicate that in the depolarised part of the light scattered by liquids, the undisplaced spectral line, if present at all, should be extremely weak, and that the whole of the depolarised light appears in the continuous spectrum of altered wave-length.

The present investigation was undertaken with the object of re-examining the same problem somewhat more carefully. It was thought desirable to repeat the work using finer slit widths so as to minimise the superposed continuous spectrum which tends to suppress the visibility of the spectrally well-defined parts of the scattered light. Further, it appeared desirable also to examine the case of highly associated liquids like acetic and formic acids, in which there is already some evidence available that molecular rotation is greatly hindered ^{2,3,4}.

Results

The three typical non-associated liquids—carbon tetrachloride, toluene and carbon disulphide—were re-examined using the finest slit widths possible, and the results obtained were found to be in agreement with those previously reported, *i.e.*, all the three spectral components observed in the spectrum of the scattered light appeared only in the vertical vibration, *viz.*, were completely polarised. In the case of the highly associated liquids—formic and acetic acids—, however, it was found that in the horizontal vibration, the scattered light showed a feeble component in the position of the central undisplaced line. The appearance of this component is probably very significant in relation to the investigations of Venkateswaran,² Bhagavantam³ and Rousset⁴ already cited, who found that the depolarisation of the scattered light when measured spectroscopically with fine and narrow slits does not differ so greatly in the case of highly associated liquids like formic and acetic acids as in non-associated liquids. Further, R. S. Krishnan⁵ has reported recently optical evidence, also based on depolarisation measurements, which indicate the presence of large clusters of molecules in these liquids. If such large clusters are present which do not rotate or oscillate freely and which depolarise the light by reason of their anisotropy of shape or structure, we should expect the Q branch of the scattered radiation, *i.e.*, the central undisplaced component, to show an appreciable

² S. Venkateswaran, *Phil. Mag.*, 1932, 14, 258.

³ S. Bhagavantam, *Proc. Ind. Acad. Sci.*, 1935, 2, 63.

⁴ A. Rousset, *C. R.*, 1933, 197, 1033.

⁵ R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1936, 3, 126.

degree of depolarisation. This is the result actually observed with the Fabry-Perot etalon. We may thus infer from the observed results that in formic and acetic acids, non-rotating clusters of molecules are present which depolarise the scattered light to an appreciable extent without changing its wave-length.

In conclusion, the author wishes to express his grateful thanks to his professor Sir C. V. Raman, for his kind interest in this work.

Summary.

The present work deals with the study of the state of polarisation of the three components observed in the spectrum of monochromatic light scattered by liquid formic and acetic acids, when examined with a Fabry-Perot etalon. It is noticed with these liquids that the central undisplaced component of the triplet observed on analysing the transversely scattered light spectrographically with a Fabry-Perot etalon shows an appreciable degree of depolarisation, differing in this respect from non-associated liquids like carbon tetrachloride, toluene and carbon disulphide, in which the central component is unobservable in the horizontal vibration of the transversely scattered light. There is thus an indication of the presence of large non-rotating or immobile clusters of molecules in these liquids which depolarise the scattered light.

INDEX TO Vol. III (A).

AUTHORS' INDEX.

- | | |
|--|---|
| Ali, Sh. Nawazish, and Samuel, R. | Absorption spectra of tetra-alkyl ammonium salts. Contributions to the theory of co-ordinate linkage—IX, 399. |
| Ananthakrishnan, R | <p>.. The Raman spectra of some organic liquids under high dispersion and resolving power (benzene, toluene, phenol, chlorobenzene, pyridine and cyclohexane), 52</p> <p>Polarisation of the Raman bands of water and deuterium oxide, 201</p> <p>The Raman spectra of propylene and iso-butane, 527.</p> |
| Asundi, R K | <p>.. Rotational analysis of the Angstrom bands at $\lambda\lambda$ 6080 and 6620 A.U, 554</p> |
| Asundi, R K, and Samuel, R. | <p>On the band systems and structure of SiF₄, 346.</p> <p>Electronic configuration and bond energy, 466.</p> <p>On the dissociation energy of carbon monoxide, 562.</p> |
| Bhagavantam, S, and Rao, A Veerabhadra | Deformation frequencies in the Raman spectra of linear molecules Acetylene, 135 |
| Bogoluboff, N | See Kryloff and Bogoluboff. |
| Born, Max | <p>.. .. Unitary theory of field and matter—I. Classical treatment Charged particle with magnetic rest-moment, 8, II Classical treatment Charged particle with electric and magnetic moment, 85</p> |
| Born, Max; and Nath, N. S Nagendra | The neutrino theory of light, 318 |
| Chowla, I. | <p>.. .. Vinogradow's solution of Waring's problem (II), 51.</p> |
| Chowla, S | <p>.. .. Pillai's exact formula for the number $g(n)$ in Waring's problem, 339.</p> |
| Dabholkar, V. D. | See Taylor and Dabholkar |
| Dhingra, D. R, Uppal, Harminder Lal; and Venkataraman, K | Antiseptics and anthelmintics—II. A synthesis of 6-benzyl-7-hydroxyflavone and 6- <i>n</i> -hexyl-7-hydroxyflavone, 206. |
| Gora, Edwin | <p>.. .. On the theory of pressure broadening of spectral lines, 272.</p> |
| Gulatee, B. L. | <p>.. .. Gravity formulæ in geodesy: their precision and interpretation, 221.</p> |
| Gupta, Hansraj | <p>.. .. On the numbers of Ward and Bernoulli, 193</p> |
| Haq, Mohd. Israrul, and Samuel, R | On the absorption spectra and linkage of inorganic nitrates and sulphates in the vapour state, 487. |

- Hirwe, N. W., and Jambhekar, M. R. Derivatives of salicylic acid—IX Stability of the sulphonic acid group in the 4-sulphosalicylic acid—
I Nitration of 4-sulphosalicylic acid, 236, X Stability of sulphonic acid group in the 4-sulphosalicylic acid—II Bromination of 4-sulphosalicylic acid, 261.
- Jambhekar, M. R. .. See Hirwe and Jambhekar
- Jogarao, Ch. V. .. Variation of intensity of scattered light with temperature, 377
- Krishnan, R. S. . Molecular clustering in liquid fatty acids, 126
Scattering of light in optical glasses, 211
Dispersion of depolarisation of Rayleigh scattering—
I Fatty acids, 566
- Kryloff, N., and Bogoluboff, N. Upon some new results in the domain of non-linear mechanics, 523
- Mehta, S. M. .. See Parmar and others.
- Narayanamurthi, D. S., and Seshadri, T. R. Brucine sulphate as an internal indicator in titrations with standard dichromate solution, 38.
- Nath, N. S. Nagendra .. See Raman and Nath
See Born and Nath
Neutrinos and light quanta, 448.
- Padhy, Brojomohan .. Pillai's exact formula for the number $g(n)$ in Waring's problem, 341.
- Parmar, M. U., Mehta, S. M., and Prasad, Mata Parthasarathy, S. Studies in thorium phosphate gels, 107
Ultrasonic velocities in some organic liquids—II, 285; III Esters and ethers, 482, IV. Halogen compounds, 519.
Ultrasonic velocities in liquid mixtures, 297.
Resonance curves for a quartz oscillator immersed in liquids, 544.
Diffraction of light by ultrasonic waves—I. 442; II Reflection and transmission phenomena, 594.
- Prasad, Mata .. See Parmar and others.
- Prasad, Sheonath . See Singh and Prasad
- Rajagopalan, V. S. On the structure and optical characters of the nacre in iridescent shells—I, 572
- Ramanadham, M. .. Optic moments of organic molecules in relation to crystalline and magnetic birefringence, 43
Refractivity and magnetic birefringence of liquid mixtures, 384
- Raman, C. V. .. First annual meeting of the Indian Academy of Sciences—Presidential Address, 1.
- Raman, C. V., and Nath, N. S. Nagendra The diffraction of light by high frequency sound waves—III Doppler effect and coherence phenomena, 75, IV. Generalised theory, 119; V. General considerations: Oblique incidence and amplitude changes, 459.

- Raman, P. K. . . . The measurement of the transmission of heat by convection from insulated ground to the atmosphere, 98
- Ram, Gurdas, and Vaidhyanathan, V. I. . . The design of falls with reference to uplift pressure, 360
- Rao, A. Veerabhadra . . . See Bhagavantam and Rao
- Rao, B. Nagesha . . . Diamagnetic susceptibility of sulphuric acid-water mixture, 188
- Rao, B. Sanjiva, and Subramaniam, K. S. . . The occurrence of Furan derivatives in volatile oils—III β -clausenan and γ -clausenan, 31
- Rao, B. Sundara Rama . . . Studies on the anisotropy of the optical polarisation field in liquids—I, II, III, 240, 244, 369
- Rao, B. V. Raghavendra . . . Doppler effect in light scattering in liquids—III Polarisation of light transversely scattered by formic and acetic acids, 607
- Rao, K. Sambasiva . . . On a function connected with the singular series, 304
- Rao, P. Suryaprakasa . . . See Seshadri and Rao
- Samuel, R. . . . See Ali and Samuel
See Asundi and Samuel
See Haq and Samuel
- Sarma, M. L. N. . . . On the error term in a certain sum, 338
- Sastri, B. N., and Sreenivasaya, M. . . . Lipins of Fenugreek (*Trigonella farnum gracum*), 513
- Seshadri, T. R. . . . See Narayanamurthi and Seshadri
- Seshadri, T. R., and Rao, P. Suryaprakasa . . . Geometrical inversion in the acids derived from the coumarins—II. *Cis* to *trans*, 293.
- Seshan, P. K. . . . The absorption spectra of some aromatic compounds—I Hydrocarbons, 148, II Quinones and hydroquinones, 172
- Seth, B. R. . . . Vortex motion in rectangular cylinders, 435.
- Siddiqui, R. H. . . . See Siddiqui and Siddiqui
- Siddiqui, S. . . . The alkaloids of *Holarrhena anti-dysenterica*—IV The occurrence of two further new bases in the bark of Indian holarrhena and their relationship to conessine and holarrhmine, 249
- Siddiqui, S., and Siddiqui, R. H. . . . The alkaloids of *Holarrhena anti-dysenterica*—V. Studies in holarrhmine, 257
- Singh, B. K., and Prasad, Sheonath . . . The physical identity of enantiomers—II. (a) The rotatory dispersion of *d*-, *l*- and *dl*-forms of isonitrosocamphor and their sodium derivatives. (b) The differences in the physiological action of *d*-, *l*- and *dl*-forms of sodioisonitrosocamphor, 586.
- Sreenivasaya, M. . . . See Sastri and Sreenivasaya.
- Subramaniam, K. C. . . . Magnetic susceptibilities of some organic compounds in different physical states, 420
See Varadachari and Subramaniam.
- Subramaniam, K. S. . . . See Rao and Subramaniam

- Tawde, N. R. . . . Intensities in the bands of the violet cyanogen system, 140
- Taylor, H. J., and Dabholkar, V. D. The tracks of the α -particles of thorium and its products, 265
- Uppal, Harminder Lal . . . See Dhingra and others
- Vaidhyanathan, V. I. . . . See Ram and Vaidhyanathan
- Varadachari, P. S., and Subramaniam, K. C. Magnetic studies of sulphur and some sulphur compounds, 428
- Venkataraman, K. . . . See Dhingra and others.
- Venkateswaran, C. S. . . . The Raman spectra of ortho-phosphoric acid and some phosphates, 25
 The Raman spectrum and electrolytic dissociation of selenic acid, 307
 The Raman spectra of selenous acid and its sodium salts, 533

TITLE INDEX (A).

- Annual meeting, first, of the Indian Academy of Sciences—Presidential address (Raman), 1
- Antiseptics and anthelmintics, II (Dhingra and others), 206.
- Bands of the violet cyanogen system, intensities (Tawde), 140.
- Band systems and structure of SiF (Asundi and Samuel), 346
- Brucine sulphate as an internal indicator in titrations with standard dichromate solution (Narayanamurthi and Seshadri), 38
- Diamagnetic susceptibility of sulphuric acid-water mixture (Rao), 188
- Diffraction of light by high frequency sound waves, III, IV, V (Raman and Nath), 75, 119, 459.
- Diffraction of light by ultrasonic waves, I, II (Parthasarathy), 442, 594
- Dissociation energy of carbon monoxide (Asundi and Samuel), 562.
- Doppler effect in light scattering in liquids, III (Rao), 607.
- Electronic configuration and bond energy (Asundi and Samuel), 466.
- Enantiomers, physical identity, II (Singh and Prasad), 586
- Falls, design, with reference to uplift pressure (Ram and Vaidhianathan), 360
- Furan derivatives, occurrence, in volatile oils, III (Rao and Subramaniam), 31
- Geometrical inversion in the acids derived from the coumarins, II (Seshadri and Rao), 293
- Gravity formulæ in geodesy; their precision and interpretation (Gulatee), 221.
- Heat, transmission by convection from insulated ground to the atmosphere, measurement (Raman), 98.
- Holarrhena anti-dysenterica, alkaloids, IV (Siddiqui), 249
- Holarrhena anti-dysenterica, alkaloids, V (Siddiqui and Siddiqui), 257
- Iridescent shells, the structure and optical characters of the nacre, I (Rajagopalan), 572.
- Light, scattered, variation of intensity with temperature (Jogarao), 377
- Light, scattering, in optical glasses (Krishnan), 211
- Light, the neutrino theory (Born and Nath), 318.
- Lipins of Fenugreek (*Trigonella foenum-græcum*) (Sastri and Sreenivasaya), 513.
- Magnetic studies of sulphur and some sulphur compounds (Varadachari and Subramaniam), 428.
- Magnetic susceptibilities of some organic compounds in different physical states (Subramaniam), 420.
- Mechanics, non-linear, some new results in the domain (Kryloff and Bogoliuboff), 523.
- Molecular clustering in liquid fatty acids (Krishnan), 126
- Neutrinos and light quanta (Nath), 448
- Optic moments of organic molecules in relation to crystalline and magnetic birefringence (Ramanadham), 43.
- Polarisation field in liquids, optical, studies on the anisotropy, I, II, III (Rao), 240, 244, 369.
- Polarisation of the Raman bands of water and deuterium oxide (Ananthakrishnan), 201.
- Quartz oscillator immersed in liquids, resonance curves (Parthasarathy), 544.
- Raman spectra of linear molecules, deformation frequencies (Bhagavantam and Rao), 135.

- Raman spectra of ortho-phosphoric acid and some phosphates (Venkateswaran), 25.
 Raman spectra of propylene and iso-butane (Ananthakrishnan), 527
 Raman spectra of selenious acid and its sodium salts (Venkateswaran), 533.
 Raman spectra of some organic liquids under high dispersion and resolving power (Ananthakrishnan), 52
 Raman spectrum and electrolytic dissociation of selenic acid (Venkateswaran), 307.
 Rayleigh scattering, dispersion of depolarisation, I (Krishnan), 566
 Refractivity and magnetic birefringence of liquid mixtures (Ramanadham), 384.
 Rotational analysis of the Ångström bands at $\lambda\lambda 6080$ and 6620 \AA. U. (Asundi), 554
 Salicylic acid, derivatives, IX, X (Hirwe and Jambhekar), 236, 261
 Singular series, on a function connected with (Rao), 304
 Spectra, absorption, and linkage of inorganic nitrates and sulphates in the vapour state (Haq and Samuel), 487
 Spectra, absorption, of some aromatic compounds, I, II (Seshan), 148, 172.
 Spectra, absorption, of tetra-alkyl ammonium salts (Ali and Samuel), 399
 Spectral lines, pressure broadening, theory (Gora), 272
 Sum, certain, error term (Sarma), 338
 Thorium and its products, the tracks of the α -particles (Taylor and Dabholkar), 265
 Thorium phosphate gels, studies (Parmar and others), 107
 Ultrasonic velocities in liquid mixtures (Parthasarathy), 297
 Ultrasonic velocities in some organic liquids, 41, III, IV (Parthasarathy), 285, 482, 519.
 Unitary theory of field and matter, I, II (Born), 8, 85
 Vortex motion in rectangular cylinders (Seth), 435
 Ward and Bernoulli, numbers (Gupta), 193
 Waring's problem, Pillai's exact formula for the number $g(n)$ (Chowla), 339
 Waring's problem, Pillai's exact formula for the number $g(n)$ (Padhy), 341
 Waring's problem, Vinogradov's solution, II (Chowla), 51.

